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Stability and Transport of Novel Engineered Nanomaterials in Aqueous and Subsurface Environments

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Stability and Transport of Novel Engineered Nanomaterials in Aqueous and Subsurface Environments

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Chemical and Environmental Engineering

by

Jacob Delano Lanphere

August 2014

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Dedication

I have dedicated this dissertation to my wife who has stood by my side and prayed for me throughout this academic journey, my daughters who have made me smile and laugh when times were stressful, and to my Lord and Savior Jesus Christ who has made all of this possible.
ABSTRACT OF THE DISSERTATION

Stability and Transport of Novel Engineered Nanomaterials in Aqueous and Subsurface Environments

by

Jacob Delano Lanphere

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, August 2014
Dr. Sharon L. Walker, Chairperson

The primary goal of this doctoral research was to investigate the environmental parameters that may influence the fate and transport of engineered nanomaterials (ENMs) in natural and engineered systems. Studies were conducted with emerging “boutique” ENMs (graphene oxide and molybdenum disulfide). The influence of environmentally relevant parameters (i.e., ionic strength, pH, presence of natural organic matter, water type (groundwater vs. surface water, and presence of divalent cations (i.e., Ca$^{+2}$, Mg$^{+2}$)) on the stability, and transport of graphene oxide was investigated. The presence of a pluronic surfactant was also studied to observe its influence on the stability, aggregate morphology, and transport in porous media for a popular transitional metal dichalcogenide molybdenum disulfide. It was hypothesized that traditional colloid filtration theory developed for spherical colloids, would accurately predict the deposition of graphene and molybdenum disulfide in aquatic systems, regardless of their unique two-dimensional planar geometry. Results from this dissertation confirm this hypothesis and provide crucial information that should be used for sustainable nanoparticle development,
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Chapter 1

Introduction
**1.1 Motivation and Background**

Nanotechnology is a rapidly developing field that has many international companies investing significant amounts of money into this exciting new technology (1). Nanotechnology incorporates the applications of materials on the nanoscale (one dimension of the material under $10^{-9}$ m) for use in many fields including sensors (2, 3), nano-medicine (4, 5), sustainable energy (6), optical (7), and electronics(8, 9) to name a few. Some of the most common nanomaterials being used in research and development for nanotechnology include metal oxides (titanium dioxide (10), cerium oxide(11), zinc oxide(12)) and carbon based (carbon nanotubes(13), fullerenes(14), graphene(15), and graphene oxide(16)) materials. With the global market demand to be greater than $3000 billion dollars by 2015 (as estimated by the commercialization of nanocomposites alone), the use and application of nanomaterials will have a tremendous impact on the global economy(17) .

While there are many positive benefits that nanotechnology will likely provide to mankind, there are also numerous uncertainties in the science community regarding its potential negative impacts (18). A report by the environmental protection agency (EPA) written in 2007 stated that “It is inevitable that during their manufacture and use, engineered nanoparticles (ENPs) will be released into the environment” (19). Furthermore, a comprehensive global life cycle analysis of ENMs by Keller et al. in 2013 also echoed this statement by the EPA and reported that 63-91% of ENMs produced in
2010 ended up in a landfill while the remaining portions ended up in the air, water, and soil (20). These reports issued by regulators and researchers highlight the demand to understand the fate and transport of ENMs once released into the environment.

Another concern regarding nanotechnology is the potential toxic impacts that ENMs will have on organisms (e.g., phytoplankton (21), mice(22), zebra fish(23), humans(24)) living in the environment or food crops (e.g., soybean (25)) that are consumed around the globe. While the toxicity of ENMs is mainly size, dose, and type dependent (26), there is still growing concern in society that bioaccumulation may occur and have dramatic consequences to organisms living in aquatic environments (27). For example, in 2012, Priester et al. reported that buildup of manufactured nanomaterials could significantly impact the quality and yield of soil based crops (25). Coupled together with the inevitable release of ENMs into the environment and their suggested toxicity from countless reports, it is crucial that the behavior of ENMs in soils and aquatic environments is well studied and understood to prevent profound negative impacts to society.

In 2013, Hendren et al. reported that the demand for environmental exposure research is increasing (28). There is currently a lack of fate and transport research to help explain the movement and behavior of ENMs in soil and aquatic matrixes. If the sustainable implementation of nanotechnology is to occur, then regulators and policy makers need to have detailed information regarding the mechanisms that control the retention, deposition, and release of ENMs under environmentally relevant conditions to
identify the potential risks of contamination in specific aquatic environments (groundwater, surface waters).

To bridge the gap regarding the lack of research and data available for ENMs fate and transport, this doctoral research investigated two novel nanomaterials (graphene oxide and molybdenum disulfide (MoS$_2$)) that are expected to have a huge impact in the field of nanotechnology (16, 29). Both graphene oxide and MoS$_2$ are two dimensional planar materials that are prized for their promising applications in the electrochemistry field (16, 30). In 2010 there were over 400 patents filed for products containing graphene (31) highlighting the tremendous interest in this material and likely future presence in the environment. Furthermore, in 2012, it was reported that the production of graphene will be 573 tonnes by 2017 and its global market demand is projected to reach close to a billion dollars by 2020(32). However, one of the major drawbacks preventing the massive application of graphene in consumer products or electronic devices is the challenge of large scale production of graphene (33). However, one of the precursors of graphene that is catching a lot of attention is graphene oxide. Graphene oxide is not a new material, in fact it has a history that goes back almost 150 years ago when it was first prepared (34). The chemical reduction of graphene oxide using processes such as the Hummer’s method(35) can generate large quantities of graphene and may solve the previous production limitations on graphene materials (33). Graphene oxide is an oxidized form of graphene(36) and exhibits a wide range of extraordinary mechanical and electronic properties (22). Graphene oxide flakes are graphene sheets with a unique heterogeneous
surface chemistry that include oxygen bearing functional groups such as carboxyl, carbonyl, epoxy and hydroxyl groups on its edges or basal planes (7, 22, 37, 38). In addition, recent advancement in synthesis methods such as density gradient ultracentrifugation have allowed for the development of graphene oxide materials with mono-disperse thickness in solution (39). With the ability to fine tune the surface of graphene oxide materials to fit many different applications, researchers have already begun developing applications for graphene oxide. Many of the proposed applications for graphene oxide include using graphene oxide nanoparticles which are graphene oxide particles with a lateral width on the nanometer ($10^{-9}$ m) scale (5, 40). For example, Chen et al, showed that graphene oxide can be used for graphene oxide-based electrodes in conjunction with DNA, proteins, enzymes and even gas molecules (16). Another popular use for graphene oxide includes the development of graphene-oxide paper for clinical applications due to its excellent antibacterial properties (41). While there are many applications (e.g. clinical, energy storage, electronic components) and forms of graphene materials, one of its precursors -graphene oxide - in the nanoparticle form has been reported to be toxic (22). In 2013, it was determined by Duch et al. that graphene oxide was the most toxic form of graphene based materials tested in the lungs of mice (22). Therefore, as a result of its toxicity to living organism, future prevalence in industry, and multi-purpose applications; graphene oxide was the form of graphene that was chosen to be investigated. In addition to graphene oxide, another two dimensional planar material is also gaining significant interest in the science community based on similar material characteristics that rival that for graphene (29). Molybdenum disulfide ($\text{MoS}_2$) is a
transitional metal dichalcogenide (TMDC) comprised of layers of molybdenum wedged between sulfur atoms and has many promising applications in micro-electromechanical and nano-electromechanical systems (42). In 2014, Stephenson et al. also suggested that MoS$_2$ nano-composites could be used for lithium ion battery applications (30). One of the main applications of MoS$_2$ has been in solid lubricants (43). However, this application results in exposure to air and water environments as a results from friction and wear from MoS$_2$ containing products (44). In 2014, it was reported by the United States Geological Survey (USGS) that the production of Molybdenum was 61,000 metric tons, with only a small amount getting recycled or recovered (45). The study by the USGS suggests that not all of the molybdenum produced will be disposed of properly and is likely that a portion will end up in the environment. In addition, a study by Ward et al., suggested that the presence of molybdenum in feed stocks may produce a physiological copper deficiency in ruminants (46).

Therefore these two ENMs (graphene oxide and MoS$_2$) were chosen since they will likely be manufactured in great amounts and have exhibited potential toxicity characteristics in the past. As seen in Figure 1.1 developed by Keller et al., a life cycle analysis for ENMs confirms that some portion of these particles will end up in the air, water, soil, or landfill as a result from being released from manufacturing, or consumer applications into wastewater treatment plants. While graphene oxide nanoparticles and MoS$_2$ were not included in the Keller et al. study, it is predicted that they will have a similar fate once their applications become widespread.
Figure 1.1: Global life cycle analysis for some common engineered nanomaterials showing their predicted path from production to disposal or release into the environment (Adapted from Keller et al. 2013).

Currently there is little known regarding the behavior of graphene oxide nanoparticles or MoS$_2$ once released into aqueous environments. As a result of this lack of knowledge, the scale of the public and environmental health threat from graphene oxide and MoS$_2$ contamination is unknown. To fill in this gap of knowledge, this doctoral research study set forth to provide insight to help identify to what degree graphene oxide nanoparticles and MoS$_2$ will be mobile across a large spectrum of aquatic conditions. From this study, the major variables that influence the movement and stability of graphene oxide nanoparticles and MoS$_2$ transport in aquatic and subsurface environments were determined. In addition, the fate (e.g. deposition on collector surfaces or retention in the pore matrix) was investigated. Finally, the understanding of graphene oxide and MoS$_2$ removal and separation was obtained to help facilitate efficient material removal practices from water (e.g. wastewater or drinking water) via engineered filter design.
It has been reported (28) in literature that there is a severe need for more studies regarding the fate and transport of engineered nanomaterials (ENMs) to help promote the sustainability and implementation of these important materials. This lack of data limits researchers and policy makers who are trying to accurately predict the path of ENMs using sophisticated models (e.g. Eularian-Lagrangian (47), Direct Simulation Monte Carlo(48)). In fact, according to Hendren et al, a recent review of the International Council of Nanotechnology (ICON) database of Nano related publications deal with 90% of toxicity and effects while only 10% of the publications are related to environmental fate and transport (28). The results from this doctoral work will help fill in the gaps for future researchers who perform fate and transport model simulations to help predict the movement of ENMs in the environment.

The ultimate goal of this study was to understand how the following elements impact the fate and transport of ENMs in aquatic and subsurface environments. Different sets of elements were considered and were broken up into separate objectives.

- The first objective was to investigate the effects of solution chemistry (i.e. pH and ionic strength (IS)) on graphene oxide nanoparticles.

- The second objective looked into different water sources and how the different constituents in each water source influence graphene oxide nanoparticles. The sources of water examined were (1) surface water (2) ground water and (3) waters with natural organic matter (NOM) present.

- For the third objective, different salt types (i.e. monovalent vs. divalent) were used to study their impacts on graphene oxide nanoparticles. The specific salts
utilized were potassium chloride (KCl) and sodium chloride (NaCl) for the monovalent salts and calcium chloride (CaCl₂) and magnesium chloride (MgCl₂) for the divalent salts.

- Objective 4 was developed to shed light on the behavior of MoS₂ as a function of its synthesis type. Lithiated molybdenum disulfide (MoS₂-Li) and pluronic (PF-87) stabilized molybdenum disulfide (MoS₂-PL) were chosen to determine which type of MoS₂ would be the least mobile during transport in saturated porous media. Both forms of MoS₂ were characterized (electrophoretic mobility, hydrodynamic diameter, and fractal dimension) as a function of ionic strength and pH and the transport in the packed bed column was investigated as a function of IS across a similar range of conditions used in objective 1.

This study involved extensive characterization of the particles including the determination of electrokinetic properties and hydrodynamic diameters of ENMs at each condition listed above to understand the transport mechanisms and stability once released into aqueous and subsurface environments. The transport study was developed based on the stability results and performed in saturated porous media through a packed bed column to simulate groundwater flow in the subsurface environment and particle deposition under conditions listed above. To date, there are very few studies that have dealt with graphene oxide fate and transport (49-51) and no studies for MoS₂. For the graphene oxide, none of the previous reports have used the experimental rigor (triplicate experiments and statistical analysis) and combination of tools (application of particle-
particle DLVO simulations, fractal dimension measurements, and non-spherical parameters (removal efficiency, $\eta_0\alpha$) to explain transport results) that were proposed and executed in this PhD research, making this a high impact study. The results from this work will help policy decision makers as well as regulatory officials understand the behavior and impact of Graphene oxide nanoparticles and MoS$_2$ if introduced into the environment.

1.2 Objective and Scope

The following is a brief description regarding details for each objective proposed and accomplished in this study. In addition a schematic was created as a reference for all of the objectives of this doctoral study as seen in Figure 1.2 below.

![Objective Matrix](image)

**Figure 1.2:** Experimental matrix including specific project objectives accomplished in this study. The first three objectives were performed using graphene oxide nanoparticles, the fourth object was accomplished using two forms (PF-87 Pluronic and Lithiated) of molybdenum disulfide (MoS$_2$).
Objective 1 (Effects of Solution Chemistry): This objective looked at how changes in ionic strength (IS) and pH affect the stability and transport of graphene oxide and MoS$_2$. Packed-bed columns were utilized here, as they have been used extensively in the past and provide a great tool in identifying the three-dimensional behavior of colloid and bacterial transport in porous media (49, 52-55).

An IS range of $10^{-4}$ to $10^{-1}$ M KCl and a pH range of 4-10 will be investigated. This pH range was chosen because it represents a wide range of relevant environmental conditions observed in various waters (e.g. ground and surface waters) (56, 57). The results and findings of this work for Graphene oxide nanoparticles were published in *Environmental Science and Technology* and can be found in Chapter 2.

Objective 2 (Effects of Water Source): To understand how the presence of multiple ions (e.g. Mg$^{2+}$ & Ca$^{2+}$) and organic constituents impact graphene oxide stability, two different water sources were selected (1) groundwater and (2) surface water. In addition, the presence of natural organic matter (NOM) was investigated with Suwannee River Humic Acid (SRHA) being used as the model NOM in this study. The results from this work were recently published in *Environmental Engineering Science* and can be found in Chapter 3.

Objective 3 (Effects of Valence): Monovalent and divalent salts were compared to see what effect each has on the transport and stability of graphene oxide. Salts used were potassium chloride (KCl), sodium chloride (NaCl), magnesium chloride (MgCl$_2$) and
calcium chloride (CaCl$_2$) for the monovalent and divalent salt respectively. The findings in this study were recently published in *Environmental Engineering Science* and can also be found in Chapter 3.

**Objective 4 (Comparison of Nanomaterial Type: An Investigation into Pluronic Coatings):** Currently, there is little known regarding the stability and transport of MoS$_2$ in porous media and there is no information regarding the different transport trends as a function of pluronic coating. It is predicted that surfactants similar to the pluronic coating used in this study will play a significant role in developing mono-disperse and stable suspensions for industrial applications of MoS$_2$ as has been applied for carbon nanotubes in the past (58). The overall goal of this objective was to fill the gap in mechanistic knowledge regarding the fate and transport of MoS$_2$ in aqueous environments and to determine which type would be least mobile. Notably, the comparison of transport and retention trends between the two types; lithiated MoS$_2$ (MoS$_2$-Li) and pluronic MoS$_2$ (MoS$_2$-PL) will provide an in depth look into the main factors behind MoS$_2$ deposition, retention, and remobilization. Complementary characterization tools also provided insight into the interaction forces and degree of aggregation in stability measurements. This work is to be submitted to *Environmental Science and Technology* and can be found in Chapter 4.
1.3 Hypotheses

The following are general hypothesis set forth to investigate in this study. It should be noted that each of these hypothesis are addressed in different chapters found in this dissertation.

*Hypothesis 1: The transport of graphene oxide and MoS$_2$ nanoparticles will be a function of their aggregation state.*

Based on mechanisms previously described by Bradford et al., “straining” is the one of the most likely mechanisms for reduced ENM transport in porous media (53, 59). Straining can be responsible for enhanced ENM removal when the ENM aggregate ($d_p$) to grain size ($d_g$) ratio ($d_p/d_g$) is greater than the theoretical limit of 0.002 (60). The straining mechanism was investigated by measuring the effective hydrodynamic diameter of graphene oxide and MoS$_2$ using dynamic light scattering and comparing the aggregate diameter to the diameter of the quartz collectors as determined by sieving. Influence of straining on transport in packed bed columns was discussed in Chapters 2 & 3 for graphene oxide and Chapter 4 for MoS$_2$.

*Hypothesis 2: It is hypothesized that once graphene oxide and MoS$_2$ are exposed to lower IS conditions, any aggregates that were retained at higher IS conditions will be released (due to break-up of aggregates and/or reduced electrostatic interactions). This phenomena has been observed for bacterial (52), colloidal (61), and quasi-spherical (titanium dioxide) (62) particles in the past, but very limited information is available (49) for two dimensional planar ENMs.*
To test this hypothesis the release of graphene oxide and MoS$_2$ from the quartz collectors in the packed bed column was investigated by injecting DI water to reduce the IS in the column. The injection of DI water would facilitate a dramatic drop in IS and increase the electric double layer for particle-particle and particle-collector interactions. The amount of particles collected after injecting DI was quantified and compared against the amount that remained in the column even after a reduction in IS. The amount of particles retained in the column was considered irreversibly attached or irreversibly strained. The influence of IS on the reversible attachment during transport in porous media using a monovalent salt (KCl) is discussed in Chapter 2 for graphene oxide and Chapter 4 for MoS$_2$.

**Hypothesis 3:** ENMs will be most mobile when they are bound up in compact aggregates with high fractal dimensions (FD = 2~3) similar to what other studies report for titanium dioxide (63).

When ENM aggregates are tightly constrained (correlating with a higher FD) they will have the capacity to travel through the pore throat of the porous media. However, once the ENM aggregates are in conditions where the electrostatic repulsion is reduced (i.e. for IS$\geq$10$^{-1.5}$ M KCl) further rapid aggregation, or looser aggregate structure, will occur resulting in a reduced mobility and transport. This hypothesis was tested by investigating the effects of solution chemistry on the FD of two types of MoS$_2$ and by correlating these findings with transport results in the packed bed column for MoS$_2$. The correlation between FD and transport results for MoS$_2$ is discussed in Chapter 4.
Hypothesis 4: The presence of any organics (Suwannee River Humic Acid, SRHA) will result in more stable graphene oxide particles, which will increase their mobility during transport.

It has been shown in the past (64) that in the presence of natural organic matter (NOM), fullerenes (C_{60}) exhibited significantly slower deposition kinetics and it is hypothesized here that the same phenomena will occur with graphene oxide. This hypothesis was investigated by measuring the change in hydrodynamic diameter and electrophoretic mobility as a function of SRHA across a range of 0.1-10 mg/L in the presence of KCl and CaCl₂. In addition, packed bed column transport experiments were conducted as a function of NOM concentration using KCl and CaCl₂ as background electrolytes as well to understand whether the presence of NOM would increase the transport of graphene oxide in saturated porous media. The influence of NOM on the fate and transport of graphene oxide in KCl and CaCl₂ was studied and is discussed in Chapter 3.

Hypothesis 5: Divalent cations present (i.e. Ca^{+2}, Mg^{+2}) in solution will contribute to reduced electrostatic double layer thickness and subsequent repulsion and graphene oxide aggregation will occur at an IS less than that what was found for monovalent salts (i.e. KCl). Furthermore, the presence of divalent ions in solution may lead to bridging or other complex formations with macromolecules (e.g. NOM) also present in solution.
This hypothesis was formed to shed additional insight into the results found from the results in objective 1 where it was determined that graphene oxide did not begin to aggregate until an IS of $10^{1.5}$ M KCl was achieved (65). However, since the ionic strength of the solution is a function of the valence of the ion present squared, the divalent ions were predicted to impact the IS by a factor of four as opposed to the monovalent ions that only impact the ionic strength by a factor of one. The comparison of monovalent and divalent ions on the stability and transport of graphene oxide were measured by comparing the hydrodynamic diameters and electrophoretic mobility as a function of IS for monovalent salts (NaCl and KCl) and divalent salts (MgCl$_2$ and CaCl$_2$). Transport in the column as a function of ion valence was also compared for graphene oxide and is discussed in Chapter 3.

Finally, it was expected that a bridging phenomenon would result in increased graphene oxide aggregation and reduced transport as a result of the oxygen functional groups interacting with divalent ions such as Ca$^{2+}$. The bridging phenomena has been reported in multiple studies that report ion valence has a significant impact on a wide variety of nanoparticle transport (i.e. carbon nanotubes, titanium dioxide, quantum dots) (66-68) and was proposed to be the case for Graphene oxide nanoparticles in this study as well. The specific bridging effects between Ca$^{2+}$ and NOM was also investigated and discussed in Chapter 3 for graphene oxide.
Hypothesis 6: The presence of PF-87 pluronic coating on MoS$_2$ will increase its transport in porous media due to the stabilizing effect of the surfactant on the diameter and electrophoretic mobility of MoS$_2$.

The effect of a stabilizing agent such as PF-87 on MoS$_2$ fate and transport was investigated by comparing the effective diameter, electrophoretic mobility, fractal dimension, and packed bed column transport results at similar pH and IS conditions to a popular type of MoS$_2$ (lithiated) created. The different effects on the fate and transport for these two types of MoS$_2$ were investigated and are reported on in Chapter 4.

1.4 Experimental Approach

This doctoral research included a comprehensive set of characterization and transport experiments to investigate and test the hypothesis proposed above in section 1.2 for graphene oxide and two types of MoS$_2$ (MoS$_2$-Li and MoS$_2$-PL). The extensive characterization of the nanoparticle used in this study were carried out by measuring the electrokinetic properties (i.e. electrophoretic mobility (EPM)), the effective hydrodynamic diameter, and fractal dimension (MoS$_2$ only) of the materials as a function of solution chemistry. Additional scanning electron microscopy (SEM) images were also taken for the nanomaterials (MoS$_2$-PL, MoS$_2$-Li, and graphene oxide) and quartz collectors to provide additional insight regarding the effects of surface morphology on their fate and transport in column experiments. The effects of environmentally relevant parameters (e.g., ionic strength, pH, water source, presence of NOM, and ion valence) on the hydrodynamic diameters and electrokinetic properties of the graphene oxide and
MoS$_2$ were performed first to identify conditions where a significant effect was occurring and then be tested in the transport experiments. Once the stability properties for the graphene oxide and MoS$_2$ were determined as a function of solution chemistry, they were used to provide insight regarding the best conditions to be used for in the transport studies. The transport studies were performed in triplicates in the packed bed column to investigate their transport in 3-D systems as a function of solution chemistry. In addition, the results from the packed bed column system were used to better understand the mechanisms responsible for deposition, adhesion, and retention during graphene oxide and MoS$_2$ transport in subsurface environments (e.g., sediment beds). To explain the contribution of aggregate morphology observed during transport, static light scattering (SLS) experiments were performed for MoS$_2$-PL and MoS$_2$-Li as a function of IS. Finally, *Derjaguin-Landau-Verwey-Overbeek* (DLVO) simulations were used to explain interactions between particles (graphene oxide and MoS$_2$) and collector surfaces during transport. Additional electrokinetic characterization of the quartz collectors as a function of IS was performed and were used in the DLVO simulations.

### 1.5 Organization of the Dissertation

This doctoral dissertation is comprised of five chapters which include the Introduction (Chapter 1) and the Conclusion (Chapter 5). Subsequent after the Introduction is Chapter 2, which includes a comprehensive discussion on the effects of solution chemistry (pH and ionic strength) on the fate and transport of graphene oxide nanoparticles in packed bed column experiments. It was determined that pH did not have
an effect on the stability (as measured in change in effective diameter and EPM) of graphene oxide across an environmentally relevant pH range of 4-9. Additionally, it was determined that a significant effect (P<0.05) on the stability and transport of graphene oxide was observed beginning at $10^{-1.5}$ M KCl. However, one of the more notable findings was that the attachment of graphene oxide nanoparticles to quartz collectors during transport was determined to be 100% reversible as a function of IS. The results from the study in Chapter 2 were published in a manuscript titled “Effects of Solution Chemistry on the Transport of Graphene Oxide Nanoparticles in Saturated Porous Media” in the journal *Environmental Science and Technology* in 2013.

In Chapter 3 the role of more complex parameters (presence of natural organic matter and divalent ions) that are ubiquitous in different water types (groundwater and surface waters) on the fate and transport of graphene oxide nanoparticles was investigated and is titled “Stability and Transport of Graphene Oxide in Groundwater and Surface Water”. Specifically, the effects of natural organic matter were studied in the presence of KCl and CaCl$_2$ and the results showed that bridging does occur in CaCl$_2$+NOM+graphene oxide suspensions which help explain the reduced transport and increased aggregate size for graphene oxide. Overall, the major finding from this part of the doctoral work was in regards to the different fates that graphene oxide will undergo as a function of the solution chemistry present in different aquatic environments. Specifically, it was determined that in artificial groundwater experiments, graphene oxide are likely to settle out as a result from the presence of divalent ions (Mg$^{2+}$ and Ca$^{2+}$) present which
contributes to the hardness, and the reduced amounts of NOM typically found in groundwater environments. Conversely, in surface water environments, graphene oxide will be more stable and transport farther as a result from the increased presence of NOM and lower amounts hardness.

Chapter 4 highlights the unique transport behavior and stability of MoS$_2$-PL and MoS$_2$-Li as a function of their synthesis type. It was determined that MoS$_2$-PL will be the least mobile form of MoS$_2$ in aquatic environments due to the interactions between the pluronic functional groups and the quartz collector surfaces. While both forms of MoS$_2$ were not 100% reversibly bound as was discovered for graphene oxide in objective 1, MoS$_2$-Li will have a greater affinity to remobilize in packed beds as a result of weak secondary minimum interactions during deposition at higher $10^{-1.5}$ M KCl. An absence of a primary energy barrier for MoS$_2$-PL and quartz surfaces resulted in lower amounts of particles being remobilized once a dramatic decrease in IS was achieved when compared to MoS$_2$-Li.

A summary of the major findings from this doctoral research are listed in Chapter 5 titled “Summary and Conclusions”. The majority of the results from the research performed in this study has been either published or is still under review. A list of manuscripts, which are in publication and were developed as a result from this doctoral research, is provided below:


1.6 References


Chapter 2

Effects of Solution Chemistry on the Transport of Graphene Oxide in Saturated Porous Media

Previously Published in *Environmental Science and Technology*, American Chemical Society, 2013.

Abstract

A transport study was performed in saturated porous media through a packed bed column to simulate fate of graphene oxide nanoparticles (GONPs) in the subsurface environment. Transport experiments, along with mass balances and column dissections, were conducted as a function of ionic strength (IS, $10^{-3}$-$10^{-1}$ M). Additionally, an extensive evaluation of the electrokinetic properties and hydrodynamic diameters of GONPs were determined as a function of IS and pH. The measured hydrodynamic diameter and the electrophoretic mobility (EPM) of GONPs indicated an insensitivity to pH, although IS did play a role. Results from a stability study indicated that the hydrodynamic diameter of GONPs was stable and unchanging at the lower range of IS ($10^{-3}$ and $10^{-2}$ M) then became unstable when IS $\geq 10^{-1.5}$ M KCl was achieved. Specifically, for IS $\geq 10^{-1.5}$ M KCl, the hydrodynamic diameter became greater and showed a larger size range of particles than at the lower IS range ($10^{-3}$ and $10^{-2}$ M). In addition, the EPM of GONPs became less negative over the IS range of $10^{-3}$ and $10^{-2}$ M KCl. Furthermore, GONPs were found to be increasingly mobile for IS $\leq 10^{-2}$ M KCl. When GONPs were passed through the packed bed column at $10^{-2}$ and $10^{-1}$ M KCl, 5% and 100% of the GONPs were retained in the column, respectively. Finally, mass balances and column dissections revealed that in the first cm of the column 7% and 95% of the GONPs were deposited at $10^{-2}$ and $10^{-1}$ M KCl, respectively, confirming that the transport of GONPs is a function of IS. The fraction of GONPs eluted during the transport experiments provides insight
into the contribution of aggregation and reversibly bound fraction of GONPs in saturated porous media.

2.1 Introduction

With the rapid growth of technology and the dramatic improvements made in production of manufactured nano materials (MNM); the future impact of nanotechnology is projected to exceed that of the Industrial Revolution (1). Recently, one of the areas of nanotechnology that has gained significant attention for its commercial, electronic, and medical applications is carbonaceous materials (e.g. carbon nanotubes, fullerenes (C<sub>60</sub>), and graphene) (2-4). Perhaps the most popular carbonaceous material that has gained tremendous momentum and has been widely accepted as the “most exciting of nano materials” since its discovery in 2004 is monolayer graphene (5). This excitement is due to the unique properties of graphene (e.g. exceptional strength, flexibility, small size and conductivity) which can be implemented in electronic devices to make them perform faster and more efficiently (6). While knowledge about graphene has been around for decades, only recently has its popularity among scientists and engineers peaked (7). In 2010 the Nobel Prize in Physics was given to Andre Geim and Konstantin Novoselov at the University of Manchester for their groundbreaking work with two-dimensional graphene (8). In addition, the production of graphene nanoparticles (GNPs) has sparked significant interest in the science community. GNPs are planar layers of carbon atoms arranged in a honeycomb shaped structure and recently, novel synthesis methods such as
density gradient ultra-centrifugation (9) have allowed the production of mono-dispersed GNPs at specific sizes and with different properties (e.g. concentrated graphene, re-suspended graphene, agglomerated graphene, and graphene oxide (GO)).

While the many applications of GNPs are numerous and interesting to think about, the behavior and environmental implications of GNPs once introduced into the environment is not yet clearly understood. In addition, the emerging public debate over the social costs and benefits as a result of the increased presence of nanomaterials found in commercial applications points out the growing concern about their potential consequences on the environment (2, 10). Moreover, the risks of manufacturing GNPs without monitoring their fate could have dramatic consequences on humans as well as the environment. For example, in a 2012 study by Priester et al. (11) a concern was raised regarding the threat of negatively impacting major global commodity food crop (i.e. soybean plants) quality and yield as a result from MNM buildup in the environment. In addition, previous studies have shown that GNPs specifically, graphene oxide nanoparticles (GONPs) are toxic and responsible for increasing mitochondrial respiration and activating inflammatory and apoptotic pathways in mice (12). Finally, earlier work investigating the toxicity of GO, reported that the effects and toxicity are dose and size dependent (13).

With knowledge of this potential health threat to both terrestrial and aqueous ecosystems, an in depth study regarding the effects of solution chemistry on the transport and stability of GONPs over a relevant range of environmental conditions (e.g. pH and ionic strength) was performed. Since other studies (14-17) have shown that these are two
critical parameters, an in depth study into the effects of pH and IS was undertaken to understand whether GONP transport is impacted by the same variables as other nanoparticles (e.g. titanium dioxide) (18).

2.2 Materials and Methods

2.2.1 Graphene Oxide

The graphene oxide nanoparticles (GONPs) used in this study were developed using the modified Hummer’s method from natural graphite flakes and were dispersed using ultra-sonication with centrifugation and contained carbonyl, hydroxyl and carboxylic functional groups (12). Previous studies have reported graphene nanoparticles to have a planar structure (9, 12). The GONPs used in this study had an average square root surface area of 179.3 ± 111.5 nm, an average height of 0.86 ± 0.21 nm and an average perimeter of 781.1 ± 502.2 nm (19). The GONPs were previously horn sonicated and dispersed in deionized (DI) water at a concentration of 1.29 mg/mL. To create 25 mg/L GONP dilutions at each ionic strength (IS) used in this study (10^{-3}-10^{-1} M), GONPs were introduced to the electrolyte and either vortexed (Fisher Scientific, Mini Vortexer) for ≥ 30 s when GONP solution volumes were ≤ 50 ml or mixed using a magnetic stir bar at ~ 350 rpm (Fisher Scientific, Model 11-800-49SHP) when GONP solution volumes were > 50 ml. Potassium chloride (KCl) was used as the background electrolyte (ACS Research Grade, Fisher Scientific, Pittsburgh, PA) for the handling of the particles in all experiments. Electrolyte and GONP solutions were prepared using DI water (nanopure water at >18.2 MΩ cm at 25°C).
2.2.2 Complimentary Characterization of Graphene Oxide Nanoparticles

The electrokinetic properties and hydrodynamic diameters were determined for GONPs using a 25 mg/L suspension across a range of pH (5-9) and IS (10^{-3}-10^{-1} M KCl) at 25°C. The average unadjusted pH of GONPs for all IS was determined to be 5.4 ± 0.4 taken after one hour of equilibration with the atmosphere. In some experiments, the pH was adjusted using HCl or KOH (ACS reagent grade chemicals, Fisher Scientific, Pittsburgh, PA). All measurements were taken immediately after the desired pH was reached. Electrokinetic characterization was performed using a ZetaPALS analyzer (Brookhaven Instruments Corp. Holtsville, NY). The average electrophoretic mobility (EPM) was determined by taking the average of five runs for three separate trials. The hydrodynamic diameter was determined using dynamic light scattering (DLS), (Brookhaven model BI-9000AT Holtsville, NY) with a 90° scattering angle and a wavelength at 661 nm. The average diameter was determined from the average of five runs taken at 2 min/run, for three trials. For statistical analysis, the student t-test was applied to data sets, where P < 0.05 indicates a significant difference at a 95% confidence level.

2.2.3 Transport Experiments

Triplicate transport experiments were conducted in a vertically oriented adjustable length borosilicate glass column (Omnilfit, Boonton, NJ) with an inner diameter of 1.5 cm and length of 5 cm. Columns were wet packed with ultra-pure quartz sand (Iota quartz,
Unimin Corp., NC). The quartz sand was sieved for the 250-300 µm fractions to obtain an average diameter \(d_{50}\) of 275 µm. Batches of the sieved sand (~700 g) were cleaned to remove any metal or organic impurities by soaking in 12 N HCl for 24 h, followed by rinsing with DI, then dried at 800 °C for more than 8 h and rehydrated by boiling for 1 h following previous protocols for sand preparation (20). Column experiments were conducted at a flow rate of 2 mL/min \((1.89 \times 10^{-4} \text{ m/s})\) which is a representative value for groundwater flow (21, 22), by using peristaltic pumps (Cole-Parmer Instrument Company, models 7553-70 and 7553-80). For each column experiment purified sand was wet packed into the glass column with average bed porosity of 0.46 ± 0.01. Once the column was packed, more than 10 pore volumes (PV) of DI water was used to flush the column which was then followed by more than 6 PV of the desired electrolyte solution for equilibration. Experiments were conducted across a wide range of IS \((10^{-3}-10^{-1} \text{ M KCl})\) at room temperature. Next, 6 PV of the 25.6 mg/L GONPs in the desired electrolyte solution were injected into the column while simultaneously being sonicated in a ultrasonic water bath (40 kHz, Branson 2510) to prevent any aggregation prior to entering the column. Following the injection of GONPs, more than 6 PV of the GONP-free electrolyte solution were injected into the column. To confirm that the GONPs retained in the column were reversibly bound, in representative experiments an additional 6 PV of DI water were injected to quantify their release. Furthermore, using a mass balance the portion of GONPs that were reversibly bound was quantified. The column effluent was collected at one minute intervals in 15 mL centrifuge tubes using a fraction collector (CF 1 Fraction Collector, Spectrum Chromatography, Houston, TX).
The effluent from the column was then immediately characterized in a spectrophotometer (DU 800 Beckman Coulter, Fullerton, CA) to obtain the effluent GONP concentration.

Wavelength scans as a function of absorbance over a GONP concentration range of 0-25 mg/L in DI water using a (DU 800 spectrophotometer) determined that the optimal wavelength for GONP concentration measurement was 228 nm (Figure 2.1).

![Wavelength Absorbance Graph](image)

**Figure 2.1**: Optimum wavelength was determined to be 228 nm for graphene oxide nanoparticles (GONPs). The absorbance of GONPs was taken at different concentrations using a spectrophotometer (DU 800 Beckman Coulter, Fullerton, CA).

A calibration curve (CC) was developed to quantify the relationship between absorbance and concentration for GONPs from 0-25 mg/L. An $R^2$ value greater than 0.99 from the CC suggests that absorbance can be directly correlated to GONP concentration (Figure 2.2).
Figure 2.2: Calibration curve for GONPs at 228 nm. An $R^2 > 0.99$ determined that absorbance can be directly correlated to concentration.

Finally, the mass of the particles in the effluent and retained in the column was determined by integrating under the breakthrough curve (and for column dissections as described next), respectively.

2.2.4 Column Dissection

Upon completion of deposition experiments, column dissections were performed to better understand the distribution of GONPs in the column during transport. The procedure for the column dissection was based upon a previously developed protocol (23). Briefly, the bottom fitting of the column was removed and by injecting the electrolyte into the column, one cm portions of the sand flowed out of the column and
were collected. The porous media remained saturated in the background electrolyte so the distribution of the GONPs was not disrupted. Each cm of the sand and GONP mixture was collected in 50 ml centrifuge tubes. The GONPs were removed from the surface of the quartz sand by adding $\geq 20$ ml of DI water or $10^{-3}$ M NaOH and vortexing for 30 s. Next, the supernatant was taken immediately to a UV Vis spectrophotometer to determine the concentration of GONPs at each cm. Finally, the mass of the sand was measured after drying in an oven for $\geq 12$ hours at a temperature $\geq 60$ °C.

Initially, transport and dissection experiments were conducted at $10^{-1}$ M KCl with either DI water or $10^{-3}$ M NaOH added to facilitate release in the sand fractions. This was done to identify whether any difference in GONPs release would occur as a function of the solution used (DI vs. NaOH). It was determined using the student t-test, at a 95% confidence level ($P > 0.05$), that there was no statistical difference between the data sets in the amount of GONP mass collected from the quartz surface (Figure 2.3) using NaOH or DI water for facilitating release from the quartz; therefore DI was used as the primary dispersing agent for the subsequent $10^{-2}$ M and $10^{-1.5}$ M KCl column dissection conditions.
Figure 2.3: Retention Profiles including the two different solvents used (DI and NaOH) to disperse GONPs deposited on quartz surface after a column experiment. A student t-test verified that there was no significant difference (P > 0.05) between the methods used. Therefore, DI water was used to collect the GONPs after running the column at 10^{-2} and 10^{-1.5} M KCl.

2.3 Results and Discussion

2.3.1 Effects of Solution Chemistry on GONPs Stability

To identify any effects of solution chemistry on GONPs in the range of solution chemistry conditions that would exist in typical aquatic environments, a comprehensive characterization study was performed. The pH range investigated was 5-9, and the IS spectrum was 10^{-3} - 10^{-1} M KCl. This broad range of conditions encompasses not only environmental conditions, but extreme conditions as well (i.e. pH 8-9 and 10^{-1.5}-10^{-1} M KCl). Since little is known regarding transport for GONPs in saturated porous media, this
preliminary characterization served to identify potentially chemically favorable and unfavorable conditions for deposition in the column. It was determined that pH did not play a significant role (P > 0.05) in altering the hydrodynamic diameter or EPM as seen in Figure 2.4. The hydrodynamic diameter of GONPs remained relatively constant at each pH. For example, at the IS of $10^{-3}$ M KCl the hydrodynamic diameter was ~235 and ~241 nm for the pH of 5 and 9, respectively. Furthermore, there was no significant difference (P > 0.05) for these pH values at the other IS as well.

**Figure 2.4:** GONPs evaluated as a function of ionic strength (KCl) and pH for electrophoretic mobility (A) and hydrodynamic diameter (B). Error bars indicate one standard deviation of at least three measurements.

In addition, the EPM was $-3.0 \pm 0.2$ and $-2.7 \pm 0.3 \, (10^{-8} \, \text{m}^2 \, \text{V}^{-1} \, \text{s}^{-1})$ for the pH of 5 and 9 respectively. The isoelectric point (IEP) for GONPs was not found in the pH range tested (from 5 to 9) which is consistent with previous studies (24-26) that report the IEP of graphene to be around pH 3.8 to 4.7 and ≤ 3 for graphene oxide (27).
This relatively minor influence of pH on GONPs' electrokinetic properties is similar to other carbonaceous materials previously studied (e.g., fullerenes (28) and carbon nanotubes (29)), which show a negligible pH effect across an environmentally relevant range of pH. This trend is different for metal oxide nanomaterials (e.g., TiO$_2$, ZnO, CeO$_2$) (18, 30, 31), which have an IEP right in the midst of the environmentally relevant pH range and can create electrostatically favorable and unfavorable conditions during their transport. When this happens there can be charge reversal or sufficient change in the magnitude of charge such that interaction forces can change from highly unfavorable and repulsive to favorable and attractive in saturated porous media. The complex surface chemistry from the oxygen-bearing functional groups could explain why the GONPs were not affected by change in pH at the conditions in this study. There are a variety of oxygen-containing functional groups on graphene oxide surfaces (32-34) with pKa’s at 4.3 and 6.6 for carboxylic groups and 9.0 for phenolic groups (35). Even though this suggests a pKa existing within the tested pH range of 5-9, there was a negligible effect on the measured EPM or hydrodynamic diameter. This is likely due to an insignificant amount of carboxylic functional groups existing on the surface of the graphene oxide and dissociating within the pH range tested. Since pH did not significantly (P > 0.05) affect the hydrodynamic diameter or EPM of the GONPs in an environmentally relevant pH range, it was determined that the transport study should be conducted at an unadjusted pH (5.4 ± 0.4).

In agreement with the anticipated influence of electrical double layer (EDL) compression (36), the IS played a significant role on both the EPM and the hydrodynamic
diameter. The hydrodynamic diameter increased with IS, while EPM had the opposite trend (Figure 2.5). For example, at an adjusted pH of 5 the hydrodynamic diameter was \( \sim 257 \) nm and then grew dramatically to \( \sim 1381 \) nm at IS of \( 10^{-2} \) and \( 10^{-1.5} \) M KCl, respectively. In addition, for IS \( \geq 10^{-1.5} \) M KCl, a larger distribution in the EPM and hydrodynamic diameter observed, which can be seen by the more sizable error bars in Figure 2.5.

Moreover, for IS \( \geq 10^{-1.5} \) M KCl the GONPs began to aggregate rapidly particularly at \( 10^{-1} \) M KCl as indicated by the diameter reaching \( \sim 5600 \) nm during characterization in the DLS instrument. This corresponds to the EPM becoming less negative with higher IS. For example, at pH 5 the EPM was \(-3.0 \pm 0.4\) and \(-1.8 \pm 0.4\) \( (10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}) \) at \( 10^{-2} \) and \( 10^{-1} \) M KCl, respectively. As there was a clear effect on EPM and GONP size as a function of IS, subsequent transport experiments were conducted across this same range of environmentally relevant IS \( (10^{-3}-10^{-1} \text{ M KCl}) \) (37). The stability/EPM analysis show

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**Figure 2.5:** GONPs at an unadjusted pH \((5.4 \pm 0.4)\) evaluated as a function of ionic strength (KCl) for electrophoretic mobility (A) and hydrodynamic diameter (B). Error bars indicate one standard deviation of at least three measurements.
that particle-particle interactions are significantly impacted by IS suggesting this would play a dominant role in transport. Hence our study was designed to test this point through 1) traditional column study, 2) release study, 3) dissection and profile analysis.

2.3.2 Transport Study

Column experiments were conducted with GONPs and the resulting breakthrough curves (BTCs) obtained across a range of IS ($10^{-2}$-$10^{-1}$ M) are presented in Figure 2.6. As Figure 2.6 illustrates, the transport of GONPs through the column was greater at the lower range of IS tested. For example, at $10^{-2}$ M KCl the breakthrough of GONPs ($C/C_0$) plateaued at 95%.

Figure 2.6: GONP breakthrough curves for experiments run in the column at 2 ml/min at room temperature ~ 23°C as a function of ionic strength. C and Co represent the influent and effluent concentration of GONPs respectively. Pore volumes 0-10 error bars indicate one standard deviation of at least three measurement; while pore volumes 10-20 represent one run at each respective IS after DI water was injected into the column.
Experiments were also conducted at an even lower IS, $10^{-3}$ M KCl, where $C/C_0$ reached 96% (data for $10^{-3}$ M KCl presented in Figure 2.7).

**Figure 2.7:** Breakthrough curves showing the additional data from the IS 10-3M KCl condition used for GONP transport in the column.

Conversely, the BTC at $10^{-1.5}$ M KCl did not plateau, but rather showed a rising portion reaching a maximum elution peak at $C/C_0$ of 53.0 ± 15.0%. The shape of the BTC at $10^{-1.5}$ M KCl suggests the rate of GONP deposition was dynamic. Similarly shaped BTCs have been reported (38) during the transport of other nanoparticles (i.e. titanium dioxide) and were attributed to reversible particle deposition onto porous media as a result of secondary energy minimum interactions as described by previous studies (39, 40).

Finally, at the highest IS tested, $10^{-1}$ M KCl, 0.3% of the injected particles were eluted ($C/C_0=0.003$). This general trend of increasing retention with IS agrees with previous colloidal and nanoparticle studies (41, 42).
The trends reported above (section 2.3.1) regarding the increasing hydrodynamic diameter with IS agree well with the observed deposition behavior. With greater GONP aggregation increased removal was observed in the column. This is in agreement with the EPM results, suggesting as the GONPs became less negatively charged with greater IS, they have the capacity to aggregate more and to increasingly interact with the quartz collectors. Similarly, as the IS increases, the charge (as determined via streaming potential) of the quartz sand becomes less negative (43), resulting in greater quartz-GONP interactions and subsequent GONP retention in the column. The combination of these two phenomena – aggregation and more attractive interaction forces – provide insight into the greater removal and overall less elution from the column.

2.3.3 Release Study

To further understand the retention mechanisms of GONP on the quartz sand surface, DI water was injected into the column following a transport experiment at each IS (see Figure 2.6.B). These BTCs correspond to an eluted mass of GONPs from those retained during the prior column experiment (Figure 2.6.A). The percentage of total mass that was recovered after the DI injection was 1.6, 52.1, and 91.2 % following initial transport experiments conducted at \(10^{-2}\), \(10^{-2.5}\), and \(10^{-1}\) M KCl, respectively. The percentage that is eluted in these experiments provides insight into the reversibly bound fraction of GONPs. The total % recovered of GONPs after flushing the column with DI was determined to be \(~ 93\%\) across the range of IS, suggesting that GONPs are reversibly
deposited at the conditions tested. These results agree with prior nanoparticle studies that have shown that near neutral or particles of lesser charge tend to be reversibly bound (44, 45).

2.3.4 Column Dissection

Following a deposition experiment in the column at each IS (without the DI release step), the column was dissected and the spatial distribution of GONPs was quantified (Figure 2.8).

Figure 2.8: Retention profiles were developed after running the column at each respective IS. Where Cin is the concentration of GONPs being injected and Cc is the concentration of the GONPs being collected after washing the sand at each dimensionless depth.

This also allows for a mass balance to be constructed (Table 2.1). Column dissections have been performed extensively in the past to understand deposition behavior of model
colloids and other nanoparticles (e.g. TiO$_2$) in porous media (18, 20, 23, 41); however, to the authors’ knowledge, column dissection has not been applied for GONPs.

**Table 2.1:** Mass balance results from column experiments, where ME, MC, MT, represent the relative mass fraction of the mass of the GONPs in the effluent, retained in the column, and the total mass injected respectively. Transport experiments were conducted at a flow rate of 2 mL/min and a GONP concentration of 25.6 mg/L at room temperature ~ 23°C.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>IS (M)</th>
<th>ME$^a$</th>
<th>MC$^b$</th>
<th>MT$^c$</th>
<th>ME/MT$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{-2}</td>
<td>0.911</td>
<td>0.104</td>
<td>1.016</td>
<td>0.897</td>
<td></td>
</tr>
<tr>
<td>10^{-1.5}</td>
<td>0.407</td>
<td>0.641</td>
<td>1.048</td>
<td>0.388</td>
<td></td>
</tr>
<tr>
<td>10^{-1}</td>
<td>0.003</td>
<td>1.086</td>
<td>1.089</td>
<td>0.003</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ ME: Fraction of mass of GONPs in effluent of mass injected  
$^b$ MC: Fraction of mass of GONPs retained in the column  
$^c$ MT: Fraction of total mass of GONPs injected

The relative fraction of the GONPs in the effluent and retained in the column is shown in Table 2.1. The mass balance accounted for 102-109% of the GONPs injected, which is similar to the recovery trends recently published in literature (18, 46, 47). Results at 10^{-2} M KCl indicate that only ~10% of the GONPs were retained in the column shown in Table 2.1. When the IS was increased to 10^{-1.5} M KCl, ~64% of the GONPs were retained. Finally, this trend was similar for the IS of 10^{-1} M KCl where results indicate that ~108% of the GONPs were retained in the column. The mass balance results obtained by dissecting the column corroborate with the transport experiments that suggest the transport of GONPs in saturated porous media is reduced at higher IS conditions due
to the combination of increased initial aggregation, greater attractive forces between particles and quartz sand, and enhanced particle-particle interactions.

These potential mechanisms can be evaluated by further analysis of the profile shape and distribution of particles along the length of the column. The profiles show that at $10^{-2}$, $10^{-1.5}$, and $10^{-1}$ M KCl the fraction of total GONPs deposited in the column retained in the first cm (at a dimensionless depth of 0.1) were 7%, 30%, and 95%, respectively. These trends corroborate the results found from the BTCs in that the transport of GONPs is predominately driven by enhanced attractive interaction forces with increasing IS. These results indicate that the vast majority of the GONPs were deposited near the inlet for the highest IS condition tested; whereas, the lower IS conditions were more evenly distributed throughout the length of the column. Another explanation can be found from classical colloidal filtration (CFT) theory that suggests that near the inlet of the column a fraction of the particle population exhibits fast deposition as explained previously (23), which would account for the steep slope observed in the top 1 cm. The greater deposition at higher IS and steep decline in concentration between dimensionless depths of 0.1 and 0.3 is in agreement with the mechanistic explanation given above that at this higher IS larger aggregation of GONPs occurs. Finally, as a result of the high IS, straining could be responsible for the steep slope near the inlet, which would corroborate with the large diameter (~ 5600 nm), found from the DLS measurements. At $10^{-1.5}$ M KCl there was a more gradual reduction in GONP concentration with depth. For example, at $10^{-1.5}$ M KCl 30%, 15%, and 9% of the
GONPs were located at the dimensionless depths of 0.1, 0.2, and 0.3, respectively. Confirmation that these aggregates are subject to additional removal via straining (45) can be found at higher IS where the GONP aggregate to grain size ratio \( (d_p/d_g) \) is equal to or above the theoretical limit. At \( 10^{1.5} \) and \( 10^{-1} \) M, the \( (d_p/d_g) \) ratio was 0.002 (the theoretical limit) (48, 49) and 0.02, respectively. This corresponds to a straining factor \( (d_p/d_g) \geq \) the theoretical limit, which agrees with the assertion made previously that straining is one of the mechanisms responsible for GONP removal in the column at high IS conditions.

2.3.5 Application of DLVO Theory

Calculations based on traditional DLVO theory (50, 51) simulating nanoparticle-quartz interactions, assuming sphere-plate geometry and a constant potential (52), indicate the existence of a secondary energy minimum which corroborates with previous work done with GONPs (44) and are shown in Table 2.3. Interactions assuming sphere-plate geometry were calculated using the following relationships. The retarded van der Waals attractive interaction energy was calculated from the following equation (53, 57):

\[
\Phi_{VDW} = -\left(\frac{A_{dd}}{6h}\right) [1 + 14h/\lambda]^{-1}
\]  

(eqn. 1)

The repulsive electrostatic double layer interaction energies were calculated using the Hogg et al. equation (52):

\[
\Phi_{EDL} = \pi \varepsilon_0 \varepsilon_r a_p \left\{ 2\psi_p \psi_c \ln \left[ \frac{1 + \exp^{-kh}}{1 - \exp^{-kh}} \right] + \left( \psi_p^2 + \psi_c^2 \right) \ln[1 - \exp^{-kh}] \right\}
\]  

(eqn. 2)

where,

\[
\Phi_{Total} = \Phi_{VDW} + \Phi_{EDL}
\]  

(eqn. 3)
**Table 2.2: Input Parameters used in DLVO calculations**

<table>
<thead>
<tr>
<th>Input parameters</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamaker constant, ( A )</td>
<td>6.26×10^{-21}</td>
<td>J</td>
</tr>
<tr>
<td>Colloid particle radius, ( a_p )</td>
<td>**</td>
<td>m</td>
</tr>
<tr>
<td>Colloid particle diameter</td>
<td>**</td>
<td>mm</td>
</tr>
<tr>
<td>dielectric wavelength, ( \lambda )</td>
<td>1.00×10^{-7}</td>
<td>m</td>
</tr>
<tr>
<td>permittivity of free space, ( \varepsilon_0 )</td>
<td>8.85×10^{-12}</td>
<td>C/Vm</td>
</tr>
<tr>
<td>relative permittivity, ( \varepsilon_r )</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>collector surface zeta potential, ( \psi_c )</td>
<td>**</td>
<td>mV</td>
</tr>
<tr>
<td>colloid surface zeta potential, ( \psi_p )</td>
<td>**</td>
<td>mV</td>
</tr>
<tr>
<td>Debye length, ( \kappa )</td>
<td>**</td>
<td>m^{-1}</td>
</tr>
<tr>
<td>Boltzeman constant, ( k )</td>
<td>1.38×10^{-23}</td>
<td>J/K</td>
</tr>
<tr>
<td>Absolute Temperature, ( T )</td>
<td>298</td>
<td>K</td>
</tr>
<tr>
<td>Ionic Strength</td>
<td>**</td>
<td>M</td>
</tr>
<tr>
<td>proton charge, ( e )</td>
<td>1.60×10^{-19}</td>
<td>C</td>
</tr>
<tr>
<td>Seperation distance, ( h )</td>
<td>0-1000</td>
<td>nm</td>
</tr>
</tbody>
</table>

*Value selected from Feriancikova et al. (44)*

**Values not shown since they are different at each IS**
Table 2.3: Results from calculations based upon DLVO and the sphere-plate assumption for graphene oxide nanoparticles and quartz collectors.

<table>
<thead>
<tr>
<th>IS (M KCl)</th>
<th>1° energy barrier (kT)</th>
<th>1° energy barrier separation distance (nm)</th>
<th>2° min depth (kT)</th>
<th>2° min separation distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^{-3}</td>
<td>259.6</td>
<td>1.5</td>
<td>-0.01</td>
<td>117.5</td>
</tr>
<tr>
<td>10^{-2}</td>
<td>113.8</td>
<td>1</td>
<td>-0.2</td>
<td>26</td>
</tr>
<tr>
<td>10^{-1.5}</td>
<td>119.9</td>
<td>1</td>
<td>-1.6</td>
<td>11.5</td>
</tr>
<tr>
<td>10^{-1}</td>
<td>138.4</td>
<td>1</td>
<td>-74</td>
<td>4</td>
</tr>
</tbody>
</table>

Values for quartz collector zeta potentials were extrapolated from literature (44) and were used in the DLVO calculations. Values for the GONP hydrodynamic diameter were experimentally measured and were used for the particle size in the DLVO calculations. Values of electrophoretic mobility (EPM) for GONPs were used to calculate zeta potentials via the Smoluchowski equation (56) and were used in the DLVO calculations.

The depth of the energy minimum at 10^{-1} M (-74 kT) is sufficiently deep as to explain the retention of GONPs during the transport studies. However, this secondary energy minimum ceases to exist when there is a chemical perturbation, notably the reduction in IS from 10^{-1} M to that of DI water. Moreover, at 10^{-1.5} M the secondary energy minimum is shallow enough (-1.6 kT) that chemical or physical perturbations render the interaction reversible offering a partial explanation of the transport results. However, the GONPs are likely interacting not only with the quartz collectors but also each other. Therefore, DLVO theory assuming sphere-sphere (53) geometry was utilized (Table 2.3) by using the following relationships.
The retarded van der Waals attractive interaction energy was calculated from the following equation (53):

\[ \Phi_{VDW} = -\left( \frac{A_d}{12h} \right) \left[ 1 - bh/\lambda \left( \ln(1 + \lambda/bh) \right) \right] \]  

(eq. 4)

Where \( b \) is a unitless constant which has a value of 5.32, (53). The Hamaker constant used for the GONPs-water-quartz system is \( 6.26 \times 10^{-21} \) (J) taken from Feriancikova et al. (44). The repulsive electrostatic double layer interaction energies were calculated using eqn. 2 however the assumption made was that the \( \psi_p = \psi_c \) and \( a_p = a_c \) since the interactions between sphere-sphere (i.e. GONP-GONP) particles was desired. It was determined a secondary energy minima was located at particle separation distances of 8nm and a depth of -26 kT for \( 10^{-1} \) M KCl. This is a substantial energy minima; whereas, for \( 10^{-1.5} \) M KCl the particles experience a notably more shallow energy well (-0.7 kT) at a distance of 15nm.
Table 2.4: Results from calculations based upon DLVO and the sphere-sphere assumption for graphene oxide nanoparticles.

<table>
<thead>
<tr>
<th>IS (M KCl)</th>
<th>$1^\circ$ energy barrier (kT)</th>
<th>$1^\circ$ energy barrier separation distance (nm)</th>
<th>$2^\circ$ min depth (kT)</th>
<th>$2^\circ$ min separation distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-1}$</td>
<td>356.2</td>
<td>1</td>
<td>-0.01</td>
<td>126.5</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>154.8</td>
<td>0.5</td>
<td>-0.1</td>
<td>25</td>
</tr>
<tr>
<td>$10^{-1.5}$</td>
<td>209.5</td>
<td>0.5</td>
<td>-0.7</td>
<td>14</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>878.1</td>
<td>0.5</td>
<td>-25.8</td>
<td>6</td>
</tr>
</tbody>
</table>

Values for the GONP hydrodynamic diameter were experimentally measured and were used for the particle size in the DLVO calculations. Values of electrophoretic mobility (EPM) for GONPs were used to calculate zeta potentials via the Smoluchowski equation (56) and were used in the DLVO calculations.

This suggests that at the $10^{-1}$ M KCl the particles experience interactions with both quartz and each other by sufficiently strong interactions as to retain them in the column, only to be released when the IS was reduced enough to eliminate these substantial energy minima. On the other hand, at $10^{-1.5}$ M KCl the secondary energy minima between the particles are weak enough that diffusion or other gentle perturbations could reverse the interactions. This explains the observed transport behavior that at the lower of these two IS conditions the particles initially were depositing and yet being increasingly released as indicated by the decreasing slope to the BTC. Overall, the application of DLVO supports the mechanistic explanation that the removal of GONPs during transport in the column was due to a combination of reversible physical (straining) and chemical (electrostatic) interactions as opposed to being a result of irreversible chemical interactions.
2.4 Environmental Implications

In this study, it has been determined that pH did not significantly impact the stability of GONPs in aqueous environments and the governing factor for transport of GONPs in aqueous porous media was IS. It has been demonstrated that the transport of GONPs in saturated porous media will be reduced at higher IS conditions due to the combination of increased aggregation and greater attractive interactions between GONPs and the quartz sand. However, since the IS of most fresh inland surface waters (37, 54) is typically less than the IS used in this study ($10^{-2}$ - $10^{-1}$ M KCl), it is presumed that the transport of GONPs will be even greater for “normal” environmental aquatic conditions. As a result, the health and vitality of inland freshwater ecosystems could be significantly impacted if GONPs are introduced. GONPs have been shown to be toxic to mice (12), arouse oxidative stress in A549 cells (13), and have shown hemolytic activity in human erythrocytes and skin fibroblasts (55). The adverse health effects; coupled together with the high mobility of GONPs at the low IS conditions found in natural surface waters, create a potential threat to existing ecosystems. In addition, for locations where the IS remains relatively high due to runoff from sources such as road salt, irrigation, or land cover alteration (54), the transport of GONPs will be low, which can result in an environmental buildup of GONPs, causing potential hotspots and damage to fragile ecosystems. In addition, the column study results indicate that GONPs can be reversibly bound in the soil. Therefore, it is projected that any GONPs trapped in the soil at high IS conditions will be released after a dilution event such as a storm or rainfall. This will
result in a highly concentrated pulse of GONPs which could have severe biological effects on aquatic life. This knowledge regarding the reduced transport of GONPs in saturated porous media as a result of increased aggregation and greater attractive interactions between GONPs and quartz sand at high IS is crucial in understanding the fate and transport of GONPs in the environment. This information should help to encourage safe handling procedures and bring to the attention of the scientific community, the risks and consequences of environmental contamination by GONPs.
2.5 References


(54) Ionic Strength; [http://www.epa.gov/caddis/ssr_ion_int.html](http://www.epa.gov/caddis/ssr_ion_int.html)


Chapter 3

Stability and Transport of Graphene Oxide Nanoparticles in Groundwater and Surface Water


Abstract

The effects of groundwater and surface water constituents (i.e. natural organic matter (NOM) and the presence of a complex assortment of ions) on graphene oxide nanoparticles (GONP) were investigated to provide additional insight into the factors contributing to fate and the mechanisms involved in their transport in soil, groundwater, and surface water environments. The stability and transport of GONPs was investigated using dynamic light scattering, electrokinetic characterization and packed bed column experiments. Stability results showed that the hydrodynamic diameter of the GONPs at a similar ionic strength (2.1±1.1 mM) was 10 times greater in groundwater environments compared to surface water, NaCl, and MgCl2 suspensions. Transport results confirmed that in groundwater, GONPs are less stable and are more likely to be removed during transport in porous media. In surface water, MgCl2, and NaCl suspensions, the relative recovery was 94±3% indicating that GONPs will be very mobile in surface waters. Additional experiments were carried out in monovalent (KCl) and divalent (CaCl2) salts across an environmentally relevant concentration range (0.1-10 mg/L) of NOM using Suwannee River Humic Acid (SRHA). Overall, the transport and stability of GONPs was increased in the presence of NOM. This study confirms that planar “carbonaceous-oxide” materials follow traditional theory for stability and transport, both due to their response to IS, valence, and NOM presence and is the first to look at GONP transport across a wide range of representative conditions found in surface and groundwater environments.
3.1 Introduction

The application of engineered nanomaterials (ENMs) in research, development, and commercial products is widespread and has been growing rapidly (1, 2). Research into the use of carbon-based nanomaterials (e.g., fullerenes (3), nanotubes (4), and graphene (5, 6)) has gained significant attention. Specifically, the use of ENMs for consumer electronic device applications (7) has grown with major companies investing significant amounts of money into the research and development of graphene (8). In 2010 the production of graphene based materials was more than 15 tons and that number was predicted to reach > 200 tons by 2011 (8). Graphene oxide nanoparticles (GONPs), an oxidized form of graphene at the nanometer scale (9), have also gained a large amount of interest since they exhibit a wide range of mechanical and electronic properties (10). For example, GONPs have been proposed to be incorporated into heavy metal detecting sensors (11), electrodes (12), and biomedical applications (13). However, recent studies have suggested that GONPs can have toxic effects on living organisms (10, 14). Moreover, increasing studies are reporting bioaccumulation of ENMs in living organisms (e.g., soybean (15), tobacco (16), and earthworms (17)). In 2006, it was reported that the ingestion of nanoparticles via drinking water or food is possible as a result of accumulation in the environment (18). To the authors’ knowledge, there is no current information regarding the concentration of GONPs present in the environment; however, as the research and development of GONPs increases, portions of these materials will inevitably end up in aqueous environments (19, 20). A recent study investigating the life cycle analysis for ENMs showed that ~80% of carbon nanotubes (CNTs) manufactured
will potentially end up in landfills (21). It is likely GONPs will have a similar fate as CNTs since they have a lot of similarities (e.g., nanometer size, carbon based structure, and application in consumer electronic devices). As a result, transport of GONPs from landfills may cause a potential threat to nearby groundwater or surface water environments. Moreover, there are growing concerns that ENMs such as GONPs will enter natural water bodies at one point in their life cycle (22).

Natural organic matter (NOM) can have a significant effect on the fate and transport of ENMs in groundwater and surface water environments (23, 24). Commonly found in natural waters, NOM is a byproduct of decaying plant material, and is typically present in dissolved form. Typical NOM levels found in most natural waters range from 0.1-20 mg/L (25, 26). The presence of NOM has been reported to have profound effects on the fate, transport, and even toxicity of ENMs (27, 28). Notably, it has been shown that the presence of NOM can reduce the toxic effect of nanoscale zerovalent iron (29) and fullerenes (30). The stability of nanoparticles has also been reported to increase in the presence of humic acid and decrease in the presence of polysaccharides (31, 32), both of which are forms of NOM. Typically, the humic fraction of the organic material (a high molecular mass compound) makes up the majority of NOM present in most natural waters (26, 33). The presence of humics has been shown to promote the transport of ENMs for metal oxides (e.g., TiO$_2$) (34), silver nanoparticles (35), and carbonaceous materials (e.g., C60 fullerenes (36), and nanotubes (37)). Similarly, the transport of 98 nm latex colloids was increased due to the adsorption of humics on the colloids and the silica collectors (38). Additionally, a recent study demonstrated that the stability of
model metal oxide nanomaterials (TiO$_2$, CeO$_2$ and ZnO) was reduced due to the adsorption of NOM on the nanoparticles (39). For carbon based materials, humic acid has been reported to greatly increase the stability of fullerene (nC60) nanoparticles as a result of steric hindrance (40). In another study, the stability of GONPs was increased in the presence of humic acid at concentrations of 1-10 mg/L Suwannee River Humic Acid (SRHA) (41). A plausible explanation for the increased transport and reduced aggregation is steric stabilization (42, 43), which involves polymers present in humic acid that increase colloidal stability at higher NOM concentrations (e.g., >1 mg/L) which are typically found in surface water environments (44). However, groundwater systems have a much lower concentration (0.1-2 mg/L total organic carbon) (Crittenden 2005). To the authors’ knowledge, there are no published articles that investigate the effects of NOM on the transport of GONPs.

In addition to NOM, groundwater and surface water environments also include a complex mixture of ions (e.g., Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, Cl$^-$, HCO$_3^-$, SO$_4^{2-}$) which can have a significant impact on the stability and transport of ENMs (45). Currently there are limited studies that investigate the effects of complex solution chemistry found in groundwater and surface water environments on the stability and behavior of ENMs (46, 47). Moreover, there are only two other studies that have been published that investigate the transport of GONPs specifically in porous media and they were under idealized conditions (e.g., in the presence of a monovalent salt such as KCl or NaCl) (48).

To address the current limitations in knowledge regarding the stability and transport of GONPs in natural waters and their subsurface environments (e.g., sediment
beds); this study systematically investigated complex interactions that are ubiquitous in the environment including the presence of NOM, presence of mono (e.g., K+, Na+) and divalent ions (e.g., Ca2+, Mg2+), and co-presence of multiple salts (e.g., MgCl2+MgSO4+KHCO3+ NaHCO3+CaCO3) to simulate solution chemistries found in groundwater and surface water environments (25). An environmentally relevant concentration range of NOM (0.1-10 mg/l SRHA) typically found in groundwater and surface waters (49) was chosen to identify the effects of NOM presence on GONP transport in saturated porous media for both mono and divalent cations. Artificial groundwater and surface water suspensions were also used to determine the fate and transport of GONPs in each respective aqueous environment. This study was set forth to bridge the current gap of understanding regarding the fate and transport of GONPs in groundwater and surface water environments by investigating a comprehensive range parameters found in those systems.

3.2 Experimental Protocols

3.2.1 Solution Chemistry

The detailed procedure used to synthesize the graphene oxide nanoparticles (GONPs) and the physical dimensions of the materials used in this study has been published previously. The resulting GONPs had a planar structure with an average perimeter of 781±502 nm, an average height of 0.9 ±0.2 nm, and an average square root of the surface area of 179 ±112 nm (10, 41). The modified Hummer’s method was used to synthesize
the GONPs used in this study and were reported to contain oxygen bearing functional groups including carboxylic, carbonyl, and hydroxyl (10).

The GONP suspensions were created at an unadjusted pH since previous studies (41, 50) have shown that there is no significant effect on stability from pH 5-9. The artificial groundwater (51) and surface water (52) suspensions were developed using recipes found in the literature and had an ionic strength (IS) of 3.78 and 1.74 mM, respectively. To compare the effects of solution chemistry at a similar IS (1.5 mM), divalent (MgCl2) and monovalent (NaCl) salts were used. Additionally, MgCl2 was investigated across an IS range of 0.3-30 mM to understand its influence on GONP stability and transport.

A concentration of 25 mg/L GONP was used in this study and was prepared by diluting a stock GONP solution into the desired background solution (e.g., CaCl2) followed by vortexing (Fisher Scientific, Mini Vortexer, Pittsburgh, PA) for 30 s. Suwannee River Humic Acid (SRHA) was used as the model NOM and a stock solution of 544 mg/L was prepared using similar methods previously described in the literature (34, 36). Briefly, dry SRHA powder was obtained from the International Humic Substances Society (IHSS, St. Paul Minnesota, USA) and was dissolved in nanopure (>18.2 MΩ at 25°C) deionized (DI) water and stirred for 2 hours in the dark. After stirring, the NOM was filtered through a 0.22 μm Millex-GP filter (Millipore Express, Cork, IRL), pH was adjusted to 5.5 using 0.1 M NaOH, and the resulting solution was stored in the dark at 4°C. More information regarding the solution preparation of the NOM solutions can be found in the Supporting Information (SI). For the GONP stability and transport studies, the following conditions were used: a monovalent salt concentration of 31.6 mM KCl in the presence of
NOM (0.1-10 mg/L) and a divalent salt concentration range of 0.1-10 mM CaCl₂ in the absence of NOM and at 1 mM CaCl₂ in the presence of NOM (0.1-10 mg/L). The KCl and CaCl₂ concentrations in the presence of NOM were chosen since they represent previously reported concentrations where GONPs are unstable (41), therefore, any stabilizing effects in the presence of NOM could be observed. All solutions made in this study were prepared with ACS research grade materials (Fisher Scientific, Pittsburgh, PA) and were prepared using DI water (nanopure water at >18.2 MΩ cm at 25°C) and were filtered through a 0.22 µm Millex-GP filter (Millipore Express, Cork, IRL) prior to use.

3.2.2 Characterization of Graphene Oxide Nanoparticles

A zetaPALS analyzer (Brookhaven Instruments, Holtsville, NY) was used to determine the electrokinetic properties of the GONPs. Triplicate electrophoretic mobility (EPM) measurements (included five measurements per run) were taken and the average was determined. Dynamic light scattering (Brookhaven model BI-9000, Holtsville, NY) was used to determine the effective hydrodynamic diameter at a scattering angle of 90° and wavelength of 661 nm. The average hydrodynamic diameter was determined from triplicate runs, which included five measurements per run taken at 2 min per run. Statistical analysis was performed to identify significant differences between data sets by using the student t-test where a 95% confidence level was confirmed when P < 0.05.

3.2.3 Transport Experiments

An inverted borosilicate glass column (inner diameter of 1.5 cm and a packing depth of 5 cm) was wet packed with high purity quartz sand (d₅₀=275 µm, Iota quartz,
Unimin Corp., NC) at a porosity of 0.45±0.02. The quartz sand was cleaned and prepared using previously described methods (53). Peristaltic pumps were used to inject solutions into the column (1.9 × 0.1 m/s) to simulate the flow of groundwater (25, 54). For each experiment the column was packed with new sand and was thoroughly flushed by injecting > 10 pore volumes (PV) of DI water followed by > 6 PV of the background solution of that particular experiment to equilibrate the system (with or without NOM). Next, 6 PV of the background solution containing GONPs were injected into the column. During transport experiments, the injection solution (containing GONPs and the background electrolyte) was sonicated in a water bath (40 kHz, Branson 2510) at room temperature (~25° C) prior to injection to prevent aggregation. Additional conservative tracer experiments were conducted using 100 mM KNO₃ to determine an average value of the hydrodynamic dispersion coefficient (D) in the columns. All transport experiments were conducted in triplicate. Further information regarding the experimental protocol for the transport experiments may be found elsewhere (50).

To compare the different effects of groundwater, surface water, presence of NOM, monovalent and divalent salt suspensions had on GONPs during transport, the removal efficiency (η₀α) and relative recovery (Rᵣ) were calculated from the breakthrough curve (BTC) results. Larger values of the removal efficiency correlate with reduced transport in subsurface environments. The removal efficiency (η₀α) is an expression that is used to explain the retention of non-spherical particles (e.g., bacteria) (55) in porous media, and was developed using the combination of the single collector contact efficiency (η₀) and the attachment efficiency (α). The single collector contact
efficiency ($\eta_0$) is a ratio of the amount of particles that collide with divided by the rate at which particles are headed for the collector (56-58). The attachment efficiency ($\alpha$) is a measure of the successful attachments that collided with the particles (59). Together, the removal efficiency ($\eta_0\alpha$) was calculated using the following equation (55, 60):

$$\eta_0\alpha = \frac{2d_c}{3(1-\Theta)\mu}\left[\ln(R_r) + \frac{\ln(R_r)^2}{Pe}\right]$$  \[1\]

The removal efficiency ($\eta_0\alpha$) is a function of the diameter of the collector ($d_c$, 275 um); length of the packed bed ($L$, 5 cm); relative recovery ($R_r$), which is the ratio of the mass of the particles collected divided by the total mass injected; porosity ($\Theta$, 0.45) (and the Peclet number ($Pe$, 65) which was determined from the following relationship:

$$Pe = \frac{vL}{D}$$  \[2\]

The Peclet number is a function of the interstitial pore velocity ($v$), length of the column ($L$), and the hydrodynamic dispersion coefficient ($D$). The hydrodynamic dispersion coefficient was determined by fitting the average of triplicate tracer BTCs to the advection-dispersion equation (Figure 3.1). The advection-dispersion equation used to model the flow in the column was:

$$\frac{\partial C_T}{\partial t} = v \frac{\partial C_T}{\partial x} + D \frac{\partial^2 C_T}{\partial x^2}$$  \[3\]

Where, $C$ is the reduced concentration (M), $t$ is time (min), $x$ is the pore volume, $v$ is the interstitial pore velocity (cm/min) and $D$ is the hydrodynamic dispersion coefficient (cm$^2$/min). The hydrodynamic dispersion coefficient obtained from the model was 0.171 cm$^2$/min, which correlated with a $Pe = 65$ for our packed bed column.
Figure 3.1: The average of triplicate tracer (100 mM KNO₃) breakthrough curves was fitted from triplicate column experiments using the advection dispersion model. A model efficiency of 0.998 was obtained for the model fits.

3.3 Results and Discussion

3.3.1 Graphene Oxide Stability

3.3.1.1 Effect of Solution Chemistry and Natural Organic Matter

The results from the characterization of the hydrodynamic diameter and electrophoretic mobility for the GONPs as a function of CaCl₂ concentration, and NOM concentration in the presence of 31.6 mM KCl and 1 mM CaCl₂ are found in Table 3.1.
Table 3.1: Electrokinetic and hydrodynamic diameter properties of GONPs in the presence of NOM at electrolyte concentrations of 31.6 mM KCl and 1 mM CaCl₂. Additional stability characterization across a concentration range of 0.1-10 mM CaCl₂ is shown in the absence of NOM for comparison.

<table>
<thead>
<tr>
<th>Solution Chemistry Conditions *</th>
<th>Electrophoretic Mobility ((10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}))</th>
<th>Hydrodynamic Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>31.6 mM KCl</strong></td>
<td>-2.7±0.1</td>
<td>1598.1±105.1</td>
</tr>
<tr>
<td>0.1 mg/L SRHA</td>
<td>-2.7±0.1</td>
<td>1159.7±63.8*</td>
</tr>
<tr>
<td>1.0 mg/L SRHA</td>
<td>-2.8±0.1</td>
<td>573.7±56.1</td>
</tr>
<tr>
<td>10 mg/L SRHA</td>
<td>-3.0±0.1</td>
<td>248.8±7.0*</td>
</tr>
<tr>
<td><strong>0.1 mM CaCl₂</strong></td>
<td>-1.7±0.3</td>
<td>225.1±8.7</td>
</tr>
<tr>
<td><strong>1.0 mM CaCl₂</strong></td>
<td>-1.6±0.1</td>
<td>2797.8±211.6</td>
</tr>
<tr>
<td>0.1 mg/L SRHA</td>
<td>-1.6±0.2</td>
<td>2453.5±211.0</td>
</tr>
<tr>
<td>1.0 mg/L SRHA</td>
<td>-1.7±0.1</td>
<td>1556.4±182.2*</td>
</tr>
<tr>
<td>10 mg/L SRHA</td>
<td>-1.8±0.1</td>
<td>273.6±7.7*</td>
</tr>
<tr>
<td><strong>10 mM CaCl₂</strong></td>
<td>-0.9±0.02</td>
<td>ND*</td>
</tr>
</tbody>
</table>

**a:** Denotes a statistically significant difference when compared to conditions without NOM  
**b:** Not Detectable (ND): Diameter observed was greater than 6µm which exceeds DLS limitations on size characterization  
**c:** Indicates conditions in the absence of natural organic matter

In a previous study (50) the effects of KCl concentration on the stability of GONPs was investigated; however, since the dominant cation present in most aquatic environments is Ca\(^{2+}\), this divalent cation was chosen to simulate more environmentally relevant conditions. In the absence of NOM, the electrophoretic mobility (EPM) of the GONPs was sensitive to the concentration of CaCl₂ over the range tested (0.1-10 mM), with EPMs varying from -1.7 to -0.9 \(10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}\). In agreement with the EPM data,
GONP aggregation was also sensitive to CaCl$_2$ concentrations as determined by the hydrodynamic diameter of the particles, which increased dramatically from 257±9 nm to a particle size greater than the detection limit (6 µm) at 0.1 and 10 mM CaCl$_2$, respectively. This increase in the hydrodynamic diameter in the presence of Ca$^{2+}$ is more substantial than what has already been reported (234±1 nm) for a monovalent salt across a similar salt concentration (1-10 mM KCl) (50). Similar effects have been seen by others (41) working with GONPs and were explained using the Schulze-Hardy rule (61), which suggests that the coagulating power of the salt as a function of its valence will have dramatic impact on the critical coagulation concentration for particles in solution from reduced electrostatic repulsion forces due to the collapse of the electric double layer.

The effects of NOM on GONP stability were also investigated in the presence of 31.6 mM KCl and 1 mM CaCl$_2$ as seen in Table 3.1. Across all NOM concentrations tested (0.1-10 mg/L), the stability of the GONPs was increased and smaller aggregates were observed for both monovalent (K$^+$) and divalent (Ca$^{2+}$) cations. The presence of NOM had a relatively minor effect on the EPM of the GONPs in 31.6 mM KCl, and no significant effect (P>0.05) in 1 mM CaCl$_2$. Chowdhury et al. observed a similar trend and suggested that the negligible effect of SRHA on the zeta potential may be due to the sorption of SRHA onto the GO surface, and claimed that steric repulsion may be the mechanism for this phenomenon (41). Others have seen similar trends in respect to the effects of IS and NOM on the stability of ENMs (62, 63). Li et al. showed that the
aggregation rate for CeO$_2$ was greater at higher KCl and CaCl$_2$ concentrations, which is similar to the trend we observed in this study for GONP and Ca$^{2+}$ suspensions (64).

While the presence of NOM did not correlate with any specific trend regarding the EPM of the GONPs, the stability was noticeably altered. In general, for all concentrations of humic acid (0.1-10 mg/L), the GONPs were more stable in the presence of NOM. In KCl, the hydrodynamic diameter was significantly (P<0.05) reduced from 1598±105 nm to 1160±64 nm with the addition of just 0.1 mg/L NOM. Overall, the diameter in KCl was dramatically reduced 249±7 nm at the highest NOM concentration of 10mg/L. This trend was the same in CaCl$_2$ suspensions in the presence of NOM where the diameter decreased in size from 2798±212 nm to 274±8 nm in 0 and 10 mg/L NOM suspensions, respectively. However, for the CaCl$_2$ suspensions, no significant difference in diameter was observed until an NOM concentration of 1 mg/L NOM was achieved, which is an order of magnitude greater when compared to the KCl suspensions in the presence of NOM.

Overall, this trend is consistent with other studies reporting the impact of NOM presence on ENM aggregation. Hyung et al. reported that the stability of carbon nanotubes increased in the presence of Suwannee River NOM (across the range of 10-100 mg/L) (65). Similarly, at the same concentration as used in this study (1 mg/L NOM), Zhang et al. reported that the propensity of metal oxide nanoparticles (e.g., ZnO, NiO, TiO$_2$, Fe$_2$O$_3$) in 0.01 mM KCl suspensions to aggregate is reduced from the negative charge imparted by the NOM (66). In the same Zhang et al. study, it was reported the negative charge imposed by NOM to the particle surface was neutralized in
the presence of Ca$^{2+}$, which agrees with the current study. This may explain why the EPM of the GONPs was not influenced as a function of NOM in Ca$^{2+}$ suspensions in this study.

### 3.3.1.2 Effects of Groundwater and Surface Water Environments

The hydrodynamic diameter and EPM of GONPs in surface water and groundwater systems were measured and are shown in Table 3.2. While the ratios and specific ions present in each respective system are different, the IS was held constant at 2.1 ±1.1 mM to avoid any potential contributions to stability since GONP sensitivity to ionic strength has been documented (48, 50).
Table 3.2: Stability results for GONPs as a function of artificial groundwater (AGW), artificial surface water (ASW), MgCl$_2$, and NaCl. The unadjusted pH of the AGW and ASW suspensions were 7.3±0.04 and 8.5±0.9, respectively. The average ionic strength for all the suspensions was 2.1±1.1 mM.

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Ionic Strength (mM)</th>
<th>Electrophoretic Mobility ($10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>Hydrodynamic Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGW</td>
<td>3.78</td>
<td>-1.9±0.1</td>
<td>2577.4±195.0</td>
</tr>
<tr>
<td>ASW</td>
<td>1.74</td>
<td>-2.2±0.2</td>
<td>240.3±5.8$^a$</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>0.30</td>
<td>-1.9±0.1</td>
<td>246.6±1.3$^a$</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>-1.7±0.2</td>
<td>260.9±16.4$^a$</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>-1.6±0.3</td>
<td>507.0±62.9$^a$</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-1.2±0.1$^a$</td>
<td>ND$^b$</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.5</td>
<td>-4.0±0.2$^a$</td>
<td>233.2±7.1$^a$</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>-3.1±0.4$^a$</td>
<td>261.8±7.5$^a$</td>
</tr>
</tbody>
</table>

$^a$: Denotes a statistically significant difference when compared to AGW.

$^b$: Not Detectable (ND): Diameter observed was greater than 6µm which exceeds DLS limitations on size characterization.

The diameter of the GONPs ranged from 240-260 nm across the various types of waters considered in this study except for AGW which had a significantly (P<0.05) higher diameter of 2577±195 nm. The larger diameter associated with the AGW suspensions may be a result of the greater presence of Ca$^{2+}$ ions in that system. It has been reported previously (41) that the Ca$^{2+}$ ions can bind with the oxygen functional groups present on the GONPs which may explain the specific increase in GONP size observed in the AGW compared to the ASW suspensions.
The presence of another commonly found divalent cation – Mg$^{2+}$ – was examined across an IS range of 0.3-30 mM as seen in Table 3.2. It was determined that the hydrodynamic diameter of the GONPs remained quite consistent (254±10 nm) at lower IS until 4.5 mM MgCl$_2$ was achieved when the GONP aggregate reached a diameter of 508±62 nm. At the highest IS tested (30 mM MgCl$_2$) the GONP diameter was greater than 6µm (see Table 3.2) suggesting that any significant sensitivity to IS occurs beyond the typical concentrations (1 mM Mg$^{2+}$) found in aqueous environments (67). These results indicate that the GONPs will be very stable in typical environmental systems, and behave similarly in groundwater and surface water environments with comparable Mg$^{2+}$ concentrations.

The EPM of GONPs in aqueous environments was measured and the results are found in Table 3.1. The EPM of the GONPs in the AGW was $-1.85\pm0.1 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. When compared to the AGW suspension, the EPM values for the ASW ($-2.19\pm0.2 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$) and MgCl$_2$ ($-1.71\pm0.2 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$) at similar IS were not significantly different (P>0.05). In the 1.5 mM NaCl solution, GONPs were significantly (P<0.05) more negatively charged than when suspended in AGW or ASW at a similar IS (3.78 and 1.74 mM, respectively). The higher negative EPM value in the presence of NaCl is in agreement with previously reported trends for GONPs that show the critical coagulation concentration occurs at a much greater IS (44 mM NaCl) than found in ground and surface waters (41). When the IS was increased to 10 mM NaCl, a decrease in the magnitude of EPM was observed with a value of $-3.11\pm0.4 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ being recorded which was significantly (P<0.05) less negative compared to the 1.5 mM NaCl
conditions. This decrease in EPM as a function of IS for GONPs in monovalent salts has also been observed in previous studies (48, 50). For the GONPs suspended in the MgCl₂ solution, EPM values were relatively consistent -1.72±0.2 (10⁻⁸ m² V⁻¹ s⁻¹) until 30 mM MgCl₂ was achieved. At 30 mM MgCl₂, the EPM was -1.22±0.1 (10⁻⁸ m² V⁻¹ s⁻¹) and was the least stable when compared to the lower IS conditions. A similar trend was observed in the other monovalent (NaCl) and divalent (Ca²⁺) systems where an increase in IS correlated with a decrease in GONP stability as would be predicted by traditional Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (68, 69).

3.3.2. Graphene Oxide Transport in Porous Media

3.3.2.1 Effects of Ca²⁺

Representative breakthrough curves (BTC) for GONP transport as a function of CaCl₂ concentration are shown in Figure 3.2. At the lowest concentration (0.1 mM CaCl₂), ~100% of the GONPs were eluted from the column. As the CaCl₂ concentration increased, a reduction in GONP transport was observed. For example, at 1 mM CaCl₂ an intermediate concentration (compared to the 100% and 0% eluted at the lowest and highest CaCl₂ concentration tested) breakthrough occurred where ~20% of GONPs were eluted from the column.
Figure 3.2: Representative breakthrough curves are shown from triplicate column experiments performed at 25 mg/L GONPs, and varying CaCl$_2$ concentrations (0.1-10 mM) at room temperature (~23°C). The error bars represent one standard deviation (n = 3).

Ripening, a phenomenon by which deposition rates increases with time (70), is a potential mechanism for the BTC shape observed at 1 mM CaCl$_2$. Liu et al. reported a similar trend for colloidal latex particles in the presence of SO$_4^{2-}$ and suggested the BTC shape was a result of the divalent cation adsorbing onto the particle surface resulting in particle destabilization (70). Moreover, Saleh et al. reported similar BTC shape at the same concentration (1 mM CaCl$_2$) for surface-modified reactive nano-iron particles and attributed it to the increased particle attachment to sand grains during transport (71). At the highest concentration (10 mM CaCl$_2$), only 0.8% of the particles were eluted from column during transport resulting in no specific BTC shape being observed. In another report, the presence of Ca$^{2+}$ was reported to reduce the mobility of aqueous fullerenes (n-C60) and fullerols due to the bridging effect by the Ca$^{2+}$ ions with negatively charged
surfaces (72). This may explain why the transport of GONPs was reduced as a function of CaCl$_2$ concentration. It is likely that bridging among the Ca$^{2+}$ ions and the oxygen functional groups (e.g., carbonyl & carboxylic) (10) on the GONPs was responsible for the decrease in transport as shown by the breakthrough curves in Figure 3.2.

Additionally, straining is likely a mechanism that contributed to the transport results in the presence of Ca$^{2+}$ ions. Straining occurs when the ratio of the particles diameter (d$_p$) and the diameter of the collector (d$_c$) is greater than or equal to the theoretical threshold of 0.002 (73, 74). At 10 mM CaCl$_2$ the (d$_p$/d$_c$) ratio was >0.02 and correlated with 1% of the GONPs being eluted from the column. This same straining mechanism for GONP removal during transport was observed in a previous study in the presence of ≥ 31.6 mM KCl (50). Therefore, the intermediate electrolyte concentration (1 mM CaCl$_2$) was chosen to investigate the presence of NOM on GONP transport since this concentration would allow for the influence of NOM to be clearly seen.

3.3.2.2 Effects of NOM

The results from the transport study in terms of the removal efficiency and relative recovery are shown in Figure 3.3.
Figure 3.3: Removal efficiency (A) and relative recovery values (B) obtained from GONPs triplicate breakthrough curve data at electrolyte concentrations of 31.6 mM KCl and 1 mM CaCl$_2$ as a function of NOM concentration.

Overall, the presence of natural organic matter decreased the removal efficiency and increased the relative recovery for both mono and divalent cations across the entire range 0.1-10 mg/L NOM tested.

For the 31.6 mM KCl suspensions, a significant difference (P < 0.05) was observed in the transport of GONPs after only 0.1 mg/L NOM was added which is likely attributed to the sorption of NOM onto favorable attachment sites. Overall, the removal efficiency did decrease by 88% and the relative recovery increased by 314% across the range of 0-10 mg/L NOM.

For the CaCl$_2$ suspensions, no significant difference (P > 0.05) in transport was observed following addition of 0.1 mg/L NOM. However, a significant difference (P < 0.05) was observed once 1 mg/L NOM was introduced, which is an order of magnitude
greater than for the KCl system. Overall, the transport of GONP increased in the presence of NOM and the removal efficiency decreased by 99% across the range 0-10 mg/L NOM. Finally, the relative recovery increased by 565% across the range 0-10 mg/L NOM.

The removal efficiencies and relative recovery values obtained in this study correlate well with the stability characterization results as well as observations of nanoparticle transport reported in the literature in the presence of NOM (75, 76). In this study, as the concentration of NOM increased, a decrease in removal efficiency and an increase in relative recovery were observed, suggesting that the presence of NOM enhances steric hindrance and subsequently particle stability during transport. This is in agreement with what was observed from the hydrodynamic diameter characterization. However, from 0.1-1.0 mg/L NOM, a larger removal recovery was observed in the CaCl₂ when compared to the KCl suspension across the same range of organic matter concentration. This difference in removal recovery may be due to a higher degree of adsorption by NOM onto the sand grains in the presence of Ca²⁺ ions. This is similar to a recent transport study where an increase in deposition of fullerenes onto humic acid and alginate coated surfaces was attributed to the complex formation of the NOM macromolecules with Ca²⁺ ions, resulting in a reduction in the charge and steric influence of the adsorbed macromolecule layers (36). This mechanism may be responsible for the observed increase in GONPs deposition in CaCl₂ as compared to KCl suspensions at the same NOM concentration. This study is the first to present the coupled factors of NOM and divalent cations that are present in ground and surface waters on the transport of
GONPs in porous media under an idealized scenario, selected to simulate environmentally relevant conditions. Notably, this is the first study to demonstrate the potential for enhanced GONP transport in natural waters in the presence of environmentally relevant NOM concentrations and the presence of K\(^+\) and Ca\(^{2+}\) ions which are ubiquitous in groundwater and surface water environments.

### 3.3.2.3 Effects of Groundwater and Surface Water Environments

The relative recovery values obtained from the transport studies show the following removal trends AGW>ASW~NaCl~MgCl\(_2\) (Figure 3.4).

**Figure 3.4:** Removal efficiency (A) and relative recovery values (B) for GONPs suspended in different water types. GONPs suspensions had the following IS, AGW(3.78 mM); ASW(1.74 mM); MgCl\(_2\)(1.5 mM); and NaCl (1.5 mM).

While the relative recovery was similar (94±3\%) for the ASW, Mg\(^{2+}\), and Na\(^{+}\) systems, there was a significantly (P<0.05) lower amount (54±4\%) of GONPs removed during transport for the AGW suspensions. These results indicate that the majority of GONPs
will likely be removed via settling in groundwater systems and be more mobile in the substrate located at the bottom of surface waters (e.g., stream beds, sediment surface). Additional transport experiments with Mg$^{2+}$ ions were performed as a function of IS to determine at what concentrations GONPs would become less mobile. Across the range of IS tested (0.3-1.5 mM MgCl$_2$), the average relative recovery was 95±1% and there was no significant difference (P>0.05). However, once an IS of 4.5 mM MgCl$_2$ was achieved, the relative recovery dropped to 12%. This reduction in transport correlates well with the decrease in stability as observed during the sizing analysis described above. Moreover, the removal efficiency was calculated from the relative recovery results to provide insight into GONP transport. The removal efficiency in AGW was ~6 times greater than in ASW confirming the initial assertion that the enhanced amount of divalent ions (e.g., Mg$^{2+}$ & Ca$^{2+}$) ions in groundwater will play a substantial role in reducing GONP transport in these environments. Additionally, the removal efficiency was 10 and 14 times greater in AGW compared to the Mg$^{2+}$ and Na$^+$ systems at a similar IS, respectively. Overall, the removal efficiency and relative recovery results suggest that the potential transport of GONPs will be the greatest in surface water stream beds since they have a lower concentration of Ca$^{2+}$ and Mg$^{2+}$ ions present. To help understand these results one may look at straining as a mechanism responsible for removal of GONPs during transport. The diameter range for particles suspended in the ASW, MgCl$_2$, and NaCl correlates with a straining factor of 0.001 which is less than the theoretical limit (73, 77) of 0.002 which suggests that the GONPs will not be removed via the straining mechanism during transport in porous media under these conditions. However, for the AGW suspensions, a
straining factor of 0.01 was observed which is far greater than the theoretical limit suggesting that straining may be a mechanism responsible for GONP removal in groundwater environments.

3.4 Summary and Conclusions

In the past, limited studies have used simple monovalent salt systems to understand the fate and transport of GONPs in porous media; therefore, more complex systems including the presence of natural organic matter, divalent ions, and a combination of ions present in groundwater and surface water was evaluated in this study. In the presence of NOM for both monovalent and divalent cations, GONPs were shown to become more stable and will therefore have the capacity to travel longer distances in the subsurface and potentially end up disrupting ecosystems or end up in the food chain from bioaccumulation (17). The presence of divalent ions (e.g., Ca$^{+2}$, Mg$^{2+}$) resulted in GONPs being less stable when compared to monovalent ions at similar concentrations in the absence of NOM. The results indicate that there is a significant difference between the behavior of GONPs in groundwater and surface water systems. Since groundwater systems typically have a higher concentration of hardness (e.g., Ca$^{+2}$, Mg$^{2+}$) and a lower concentration of NOM, GONPs will tend to become less stable and will eventually settle out or be removed in these subsurface environments. Conversely, for surface waters, where the presence of NOM is greater and the concentration of divalent ions is typically lower, GONPs will remain stable and their transport will be greater in the subsurface layers in natural water bodies. As a result, benthic organisms
living on (or in) the sediment surfaces will likely be negatively impacted by the presence of GONPs. This study has incorporated many levels of complexity to simulate the complex conditions in environmental systems such as groundwater and surface waters and is the first to report their impact on the transport of GONPs in porous media.
3.5 References


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(22) Hammes, J.; Gallego-Urrea, J. A.; Hassellöv, M., Geographically distributed classification of surface water chemical parameters influencing fate and behavior of


Chapter 4

Fate and Transport of Molybdenum Disulfide Nanoparticles in Sand Columns

Abstract

Research and development of two-dimensional transition metal dichalcogenides (TMDC) (i.e., molybdenum disulfide (MoS$_2$)) in electronic, optical, and catalytic applications has been growing rapidly. However, to date there is little known regarding the behavior of these particles once released into aquatic environments. Therefore, an in depth study regarding the aggregate fate and transport of two popular types of MoS$_2$ nanoparticles - lithiated (MoS$_2$-Li) and Pluronic PF-87 dispersed (MoS$_2$-PL) - was conducted in saturated porous media (quartz sand) to identify which form would be least mobile in aquatic environments. The electrokinetic properties and hydrodynamic diameters of MoS$_2$ as a function of ionic strength (IS) and pH were determined using a zeta potential analyzer and dynamic light scattering techniques. Additionally, the fractal dimensions of the MoS$_2$ were characterized from 0.1-100 mM KCl using static light scattering. Results suggest that the stability is significantly (P<0.05) decreased beginning at 10 and 31.6 mM KCl, for MoS$_2$-PL and MoS$_2$-Li, respectively. Transport study results from breakthrough curves, column dissections, and release experiments suggest that MoS$_2$-PL exhibits a greater affinity to be irreversibly bound to quartz surfaces as compared to the MoS$_2$-Li at a similar IS. Derjaguin-Landau-Verwey-Overbeek (DLVO) theory was used to help explain the unique interactions between the MoS$_2$-PL and MoS$_2$-Li surfaces between particles and with the quartz collectors. The application of DLVO suggests that blocking is the dominant removal mechanism for MoS$_2$-PL as indicated from a minimal energy barrier (0-24 kT) between MoS$_2$-PL and quartz collectors and irreversible attachment.
during transport; while straining is the dominant mechanism for MoS$_2$-Li removal in the column as indicated by a secondary energy minimum and greater remobilization compared to the MoS$_2$-PL. The FD characterization suggest that more densely packed MoS$_2$-Li aggregates exists in suspensions with IS <1 mM KCl, and have a more open structure for 1-100 mM KCl. Overall, the results suggest that the fate and transport of MoS$_2$ is highly dependent on the type of MoS$_2$ that enters the environment, where MoS$_2$-PL will be least mobile and more likely be deposited in porous media from pluronic-quartz interactions and physical wedging effects while MoS$_2$-Li will travel greater distances and have a greater tendency to be remobilized in sand columns.

4.1 Introduction

Two dimensional nano-materials have gained a significant amount of attention recently (1). The most common two dimensional material has traditionally been graphene (2) or its oxidized derivative graphene oxide (3). However, research and development of molybdenum disulfide (MoS$_2$), a two dimensional transition metal di-chalcogenide (TMDC) has been increasing over the last few years (4) and is beginning to rival the popularity of graphene for monolayer materials (5). In 2012, an editorial in the journal Nature noted that “Graphene is Not Alone” and that TMDCs are gaining a tremendous amount of attention with tungsten disulfide (WS$_2$) and molybdenum disulfide (MoS$_2$) leading the way for future optical and electronic applications.(6) MoS$_2$ is a layered TMDC which includes two planes of sulfide (S) atoms with a mono plane of
molybdenum (Mo) atoms in the center of the structure with the Mo and S atoms being bound together by covalent bonds (7). The rise in popularity with MoS\textsubscript{2} may be due to its many novel electrical and optical properties (8) including a tunable band gap (9), exceptional photo-response (9), and high charge carrier mobility (10). MoS\textsubscript{2} is also a direct band gap semiconductor (11) which could make it an ideal material for transistors or to be incorporated into optoelectronics devices (12). Other applications for MoS\textsubscript{2} range from the use in lithium ion batteries (13), electrochemical charge storage (14), lubricants (15), and ultra-fast photonics (16). With the widespread research and development of engineered nanomaterials, the implementation of MoS\textsubscript{2} nanoparticles (NPs) has also gained a tremendous amount of interest for use in nano-technological applications (e.g., catalysts, and nanotubes) (17). While the production and development of MoS\textsubscript{2} NPs has a tremendous potential to provide positive benefits for society, there is a lack of knowledge and research regarding its behavior if released into the environment. To the authors’ knowledge, there are no reports that investigate the fate or transport of MoS\textsubscript{2} in aquatic environments.

In the past, it has been reported that other two dimensional nanomaterials (i.e., graphene oxide) can exhibit toxic effects on living organisms (e.g., increased mitochondrial respiration in mice) (18). Currently there is little information regarding the potential toxicity of MoS\textsubscript{2} NPs. In 2011, Wu et al. reported that inorganic fullerene-like MoS\textsubscript{2} NPs prepared using pulsed laser ablation (PLA) were biocompatible and provided a green method to synthesize nanomaterials (19). However, it has been reported in the past that elevated levels of Molybdenum (Mo) in ruminate intake can result in a physiological
copper (Cu) deficiency which may have negative consequences (20). In 2013, Keller et al. reported that it is highly likely some portion of engineered nanomaterials that reach a landfill will make their way into the surrounding environment (21). In 2014, Conway et al. reported that phytoplankton sorbed engineered nanomaterials (CeO₂) in less than 1 hour and had negative impacts on marine mussels in seawater environments (22). This suggests that if the careful implementation of nanomaterials is not employed, then their accidental release into the environment may occur and have long lasting effects on aquatic life. Therefore, it is crucial that the science community and policy makers have a comprehensive set of research data to help predict the fate and transport of MoS₂ NPs once introduced into aquatic environments.

It has been shown in recent studies (23) that the behavior of two-dimensional nanomaterials (i.e., graphene oxide) is significantly impacted by environmental parameters such as ionic strength, divalent cations (i.e., Ca²⁺), and presence of natural organic matter (24). This study set forth to bridge the gap of knowledge regarding the influence that environmentally relevant parameters (i.e., ionic strength, and pH) will have on the fate, transport, and aggregate morphology of two forms of MoS₂ NPs; Lithiated (MoS₂-Li) and Pluronic (MoS₂-PL). Therefore the MoS₂-Li was chosen since this represents the most scalable and controllable synthesis method for monolayer MoS₂ that will likely be used in the future, therefore representing the most abundant form of MoS₂ that would be found in the environment. Additionally, it is predicted that for industrial applications, a stable and mono-disperse suspension of MoS₂ will be required and therefore surfactants will play an increasing role in MoS₂ nanotechnology development.
Recent studies have also used pluronic surfactants to stabilize carbon nanotubes (25). Therefore, in this study Pluronic PF-87 was chosen as a representative surfactant as an additional form of MoS$_2$ to investigate its behavior in aquatic environments. The pluronic PF-87 triblock copolymer is a linear molecule containing a central hydrophobic chain of polypropylene oxide (PPO) functional groups and is bordered by two hydrophilic chains of polyethylene oxide (PEO) of equal length (26). Additionally, the fractal dimension of MoS$_2$ has been investigated to understand whether there exists a correlation between the aggregate morphology and the transport results for MoS$_2$ in sand columns. Other studies have suggested that the aggregate morphology may play an important role in movement and behavior of engineered nanomaterials in natural systems (27, 28).

This study is the first to report the effects of two important environmentally relevant parameters (i.e., ionic strength and pH) on MoS$_2$ NPs stability and transport in a packed bed column and provides critical information regarding how interactions between quartz surfaces influence the transport of MoS$_2$-PL and MoS$_2$-Li. This report also helps to answer the question of whether traditional colloid filtration theory can apply to these boutique nanoparticles, the planar transition metal dichalcogenides (TMDCs). The results from this report help to explain the behavior of MoS$_2$ in engineered or natural systems where they may settle or deposit on sediments in the subsurface and sheds light on the chemical and physical mechanisms responsible for this behavior. It reports the effects of two important environmentally relevant parameters (i.e., ionic strength and pH) on MoS$_2$ NPs stability and transport in a packed bed column and provides critical information
regarding how interactions between quartz surfaces influence the transport of MoS$_2$-PL and MoS$_2$-Li. This report also helps to answer the question of whether traditional colloid filtration theory can apply to these boutique nanoparticles, the planar transition metal dichalcogenides (TMDCs). The results from this report help to explain the behavior of MoS$_2$ in engineered or natural systems where they may settle or deposit on sediments in the subsurface and sheds light on the chemical and physical mechanisms responsible for this behavior.
4.2 Materials and Methods

4.2.1 Molybdenum Disulfide

The lithiated MoS$_{2}$ (MoS$_{2}$-Li) used in this study had an mean square root surface area of $(187.5 \pm 126.9 \ \text{nm})^2$, an mean height of $3.9 \pm 0.6 \ \text{nm}$ and a mean perimeter of $689.1 \pm 433.0 \ \text{nm}$. While the pluronic MoS$_{2}$ (MoS$_{2}$-PL) used in this study had a mean square root surface area of $(27.6 \pm 15.6 \ \text{nm})^2$, an average height of $5.2 \pm 1.1 \ \text{nm}$ and an average perimeter of $100.8 \pm 57.3 \ \text{nm}$. The MoS$_{2}$-PL and MoS$_{2}$-Li were previously dispersed in deionized (DI) water at stock concentrations of 0.125 and 0.038 mg/mL, respectively. To create 10 mg/L MoS$_{2}$ dilutions at each ionic strength (IS) used in this study ($10^{-4}$-$10^{-1} \ \text{M KCl}$), MoS$_{2}$ NPs were introduced to the electrolyte and either vortexed (Fisher Scientific, Mini Vortexer) or lightly shaken for $\geq 5$ s. Potassium chloride (KCl) was used as the background electrolyte (ACS Research Grade, Fisher Scientific, Pittsburgh, PA) in all experiments. The unadjusted pH of the MoS$_{2}$-Li and MoS$_{2}$-PL stock suspensions were $3.9\pm0.1$ and $5.3\pm0.1$, respectively. Potassium hydroxide (KOH) and hydrochloric acid (HCl) were used to adjust the pH of the MoS$_{2}$ suspensions. All MoS$_{2}$ suspensions were created using DI water (nanopure water at $\geq 18.2 \ \text{M} \Omega \ \text{cm at 25}^\circ\text{C}$).
4.2.2 General Characterization of Nanomaterials and Porous Media

Electrokinetic properties and hydrodynamic diameter of MoS$_2$

The influence of pH and ionic strength (IS) on the MoS$_2$-PL and MoS$_2$-Li was determined by measuring the effective hydrodynamic diameter and electrophoretic mobility (EPM) across an environmentally relevant pH range of 4-10 and an IS range of 0.1-100 mM KCl, respectively. Dynamic light scattering (Brookhaven model BI-9000, Holtsville NY) measurements taken at a wavelength of 661 nm and a scattering angle of 90° were used to determine the effective hydrodynamic diameter of the MoS$_2$ suspensions. The EPM was measured using a ZetaPALS analyzer (Brookhaven Instruments, Holtsville, NY). Triplicate measurements were taken at room temperature (23±1°C) for all of these electrokinetic and size measurements.

Aggregate Morphology of MoS$_2$

The fractal dimensions (FD) of the MoS$_2$-Li and MoS$_2$-PL as a function of IS (0.1-100 mM KCl) were measured using a multi angle static light scattering (BI-200SM, Brookhaven Instruments, Holtsville, NY) at a wavelength of 633 nm across a scattering angle of 60-135° using 15° increments. Triplicate measurements were taken at 26°C and borosilicate glass tubes were used as the sample cuvettes. The FDs were obtained from the scattering intensities using the Rayleigh-Gans-Debye (RGD) theory and previously described methods (27, 29).

\[ I(q) \propto q^{-FD} \]  \hspace{1cm} (1)
\[ q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \]  

Where; \( I(q) \) is the scattering intensity as a function of the scattering wave vector; \( q \) is the scattering wave vector; \( FD \) is the fractal dimension; \( \lambda \) is the wavelength of incident light; and \( \Theta \) is the scattering angle. The fractal dimension (\( FD \)) of the MoS\(_2\) aggregates was obtained from the slope of the line where inverse of intensity of the light scattered (\( \log(I) \)) was plotted against the scattering vector (\( \log(q) \)). A non-integer \( FD \) value from 1-3 suggests that the aggregating particles may be fractal with the lower FD values correlating with a lower packing density, typically being a result of fast aggregation occurring amongst similar particles; with the upper spectrum correlating with a maximum density of the aggregate structure as a result from slower aggregation processes (27,30).

**Elektrokinetic Characterization of Quartz**

Additional characterization of the quartz sand collectors was performed to help explain any potential interactions between the MoS\(_2\) particles and the quartz surfaces during transport in the packed bed column and was used in the application of DLVO theory. The streaming potential of the quartz sand (used as the porous media in the column experiments) was measured using a streaming potential analyzer (surPASS, Anton Paar, Graz, Austria). Triplicate measurements were taken in deionized water at pH 5 and across the same range of ionic strength (1-31.6 mM KCl) conditions used in the transport experiments.
Scanning Electron Microscope Images of MoS$_2$ and Quartz

Scanning Electric Microscopy (SEM) images were taken of the dried-aggregated MoS$_2$ nanoparticles on quartz slides. MoS$_2$ samples were prepared by adding ~15 μL of stock MoS$_2$-PL and MoS$_2$-Li at an unadjusted pH, in deionized water to quartz slides and were let to dry overnight before taking SEM images. SEM images of the quartz sand used as porous media in the column experiments were also taken. Quartz samples were prepared by adding a small amount ~30 sand grains in deionized water to a quartz slide and let dry overnight.

4.2.3 Packed Bed Column Transport Experiments

The effects of ionic strength (1-31.6 mM KCl) on the transport of MoS$_2$-Li and MoS$_2$-PL in saturated porous media was conducted using a packed bed column at pH 5. Transport experiments were conducted using an inverted borosilicate glass column (Omnifit, Boonton, NJ) with an inner diameter of 1.5 cm and a packing depth of 5 cm. Details regarding the packed bed column transport methods, conditions, and sand cleaning procedures can be found elsewhere (23) Briefly, quartz sand was sieved to obtain an average diameter ($d_{50}$) of 275 μm and purified before being wet packed at a porosity of 0.47±0.01 in the column prior to transport experiments. MoS$_2$ suspensions were injected into the column at a flow rate of 2 mL/min to represent similar flow conditions found in the engineered or natural systems (31) using peristaltic pumps and the effluent was collected every minute using a fraction collector (CF 1 Fraction Collector, Spectrum Chromatography, Houston, TX). The effluent was used to determine the concentration at
each time interval using a spectrophotometer (DU 800 Beckman Coulter, Fullerton, CA) to correlate the absorbance with concentration. Calibration curves (Figures 4.1 and 4.2) for the MoS$_2$-Li and MoS$_2$-PL were created by measuring the absorbance as a function of MoS$_2$ concentration and an R$^2$ value of 0.999 was obtained for both types of MoS$_2$.

**Figure 4.1:** Optimum wavelength was determined to be 247 nm for molybdenum disulfide Lithiated (MoS$_2$-Li) nanoparticles. The absorbance of MoS$_2$-Li was measured across a range of concentrations using a UV-Vis spectrophotometer (DU 800 Beckman Coulter, Fullerton, CA). An R$^2 > 0.99$ confirmed that absorbance was directly correlated to MoS$_2$-Li concentration.
Figure 4.2: The optimum wavelength was also determined for molybdenum disulfide pluronic (MoS$_2$-PL) nanoparticles, and was 258 nm. The absorbance of MoS$_2$-PL was also determined over a range of concentrations and an $R^2 > 0.99$ confirmed that absorbance can be directly correlated to the concentration of MoS$_2$-PL.

Release experiments were also conducted following select transport experiment at each IS for MoS$_2$-PL and MoS$_2$-Li to investigate the release of particles as a function of the decrease in IS. To facilitate the release experiments, an additional 12 PV of DI water was injected into the column after the background absorbance dropped to ~0 and the effluent was collected and the absorbance measured as mentioned earlier.

4.2.4 Column Dissection

In order to evaluate the distribution by which MoS$_2$ was retained in the column, select columns were dissected following a transport experiment. Deposition profiles of MoS$_2$ at each cm in the column were developed from the column dissections to interpret the
distribution of MoS$_2$ following an experiment at each ionic strength. The procedure for the column dissection can be found elsewhere (23) and was based upon a previously developed protocol (32). Briefly, once the experiments were completed, the bottom fitting of the column was removed and the background electrolyte was injected into the column. Next, the sand slowly flowed out of the column by gravity and approximately one cm portions of the sand were collected in centrifuge tubes as they came out of the column. The collected samples – comprising of quartz, KCl, and retained MoS$_2$ particles – were rinsed with 25 ml of DI water and vortexed for 30 s. The supernatant from this step decanted into a centrifuge tube and saved for further analysis. This step was repeated twice to achieve a total volume (50 ml) of reversibly bound MoS$_2$. These MoS$_2$-containing supernatant suspensions were then taken to a spectrophotometer to measure the absorbance of the MoS$_2$-PL and MoS$_2$-Li suspensions obtained for each cm at wavelengths of 258 and 247 nm, respectively. The absorbance values for the supernatant collected at each cm were then correlated with MoS$_2$-PL and MoS$_2$-Li concentrations using the same calibration curves mentioned previously. The remaining sand at each cm from the dissected column was then dried and the mass was recorded. Results were then plotted as the mass of nanoparticles retained in each cm of sand [(mass of MoS$_2$ retained/mass of MoS$_2$ injected)/ mass of quartz sand] dissected as a function of the depth of the column. These retention profiles were then developed to further understand the deposition behavior of MoS$_2$ throughout the column as a function of ionic strength.
4.3 Results and Discussion

4.3.1 Effects of pH and Ionic Strength on MoS$_2$ Stability

To investigate the behavior of two leading MoS$_2$ nanomaterials to identify which one is least mobile in the environment; MoS$_2$-PL and MoS$_2$-Li were extensively characterized. It has been reported in the past (33-35) that nanoparticle size (36), surface charge (37), and aggregate morphology (29) characterization can provide critical insights into predicting the ultimate fate of these materials in the environment. Therefore, a comprehensive study was performed to investigate the effects of solution chemistry on MoS$_2$-Li and MoS$_2$-PL across an environmentally relevant range of aquatic chemistries and the results are shown in Figures 4.3-4.6 and Table 4.1.
Figure 4.3: MoS$_2$-PL evaluated as a function of pH for effective hydrodynamic diameter and electrophoretic mobility. MoS$_2$-PL concentration was maintained at 10 mg/L and 10 mM KCl. Error bars indicate one standard deviation of triplicate measurements.

The pH range studied was 4-10, and the IS spectrum was 0.1 -100 mM KCl. This wide range of solution chemistry covers not only environmental conditions for most natural water (e.g., lakes, and streams) (31,38), but extreme conditions as well (i.e., pH 9-10 and 31.6-100 mM KCl) (31). The influence of pH on the diameter and EPM varied between the two types of MoS$_2$ tested as a function of their type.
Figure 4.4: MoS$_2$-PL evaluated as a function of ionic strength for effective hydrodynamic diameter and electrophoretic mobility. MoS$_2$-PL concentration was maintained at 10 mg/L and at an adjusted pH 5. Error bars indicate one standard deviation of triplicate measurements.

While it was expected that the size and surface charge of MoS$_2$-PL would not significantly change across the environmental pH range (5-9) tested due to the surfactant PF-87 coating present, it was not known what the behavior would be at the lower and upper pH values (4, 10). In addition, it was anticipated that MoS$_2$-Li would not be sensitive to pH (from 4-10) with respect to its diameter size and EPM as has been reported previously for other two-dimensional nanomaterials (e.g., graphene oxide) (35). Overall this hypothesis was correct and there was little effect on the effective diameter and EPM of MoS$_2$ as a function of pH within environmentally relevant parameters (pH 5-
It was only when the pH was near or outside of this range when a significant difference in stability for MoS\textsubscript{2}-Li and MoS\textsubscript{2}-PL was observed.

**Figure 4.5:** MoS\textsubscript{2}-Li evaluated as a function of pH for effective hydrodynamic diameter and electrophoretic mobility. MoS\textsubscript{2}-Li concentration was maintained at 10 mg/L and 10 mM KCl. Error bars indicate one standard deviation of triplicate measurements.

The effective diameter for MoS\textsubscript{2}-Li (as measured by DLS) was much more sensitive to the change in pH than anticipated. Specifically, at pH 4, the effective diameter (401±106 nm) for MoS\textsubscript{2}-Li was ~25% larger than the effective diameter (298±12 nm) at pH 5 as seen in Figure 4.5. However, there was no significant effect (P>0.05) on the MoS\textsubscript{2}-Li EPM across the range of pH (4-10) tested (See Figure 4.5). Similar results have been reported for other planar nanomaterials (e.g., graphene oxide) where no significant effect on EPM or diameter was observed from pH5-9. However, in recent studies(2014), the zeta potential of spherical nanoparticles (ZnO (39), Ag (40), and TiO\textsubscript{2} (41)) were shown to be sensitive to changes in pH across an environmentally relevant range (5-9). For the
MoS$_2$-PL, the opposite trend occurred when compared to the MoS$_2$-Li in regards to the influence on diameter and EPM. Specifically, there was no significant effect (P>0.05) in the diameter from pH 4-10, however, the EPM did significantly increase from $-0.9\pm0.1$ to $-1.4\pm0.1$ ($10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$) at pH 8 and 9, respectively.

Figure 4.6: MoS$_2$-Li evaluated as a function of ionic strength for effective hydrodynamic diameter and electrophoretic mobility. MoS$_2$-Li concentration was maintained at 10 mg/L and at an adjusted pH 5. Error bars indicate one standard deviation of triplicate measurements.

These results suggests that the MoS$_2$-PL will be the most stable across an environmentally pH range (5-9) in natural waters and will not likely be removed during transport in sediment beds since the effective diameter will remain small as a result of the PF-87 coating. However, for the MoS$_2$-Li, the sensitivity to low pH (<5) with respect to the increase in effective diameter, may result in the MoS$_2$-Li being settled out or removed sediments.
Table 4.1: Fractal dimensions of MoS$_2$-PL and MoS$_2$-Li as a function of ionic strength (0.1-100 mM KCl at an adjusted pH 5). Mass balance results from column experiments are also shown, where $M_E$, $M_D$, $M_R$, and $M_T$, represent the relative mass percent of the mass of the MoS$_2$ in the effluent, deposited mass recovered from column dissections, remobilized mass after DI injection, and the total mass collected. Transport experiments were conducted using a MoS$_2$ concentration of 10 mg/L and a flow rate of 2 mL/min.

<table>
<thead>
<tr>
<th>MoS$_2$</th>
<th>Ionic Strength (mM)</th>
<th>Fractal Dimension</th>
<th>$M_E$ (%)$^a$</th>
<th>$M_D$ (%)$^b$</th>
<th>$M_R$ (%)$^c$</th>
<th>$M_T$ (%)$^d$</th>
</tr>
</thead>
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<tr>
<td>MoS$_2$-PL</td>
<td>0.1</td>
<td>0.94±0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td></td>
<td>1</td>
<td>0.96±0.01</td>
<td>96.7±1.0</td>
<td>19.2</td>
<td>18.8</td>
<td>115.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.71±0.04</td>
<td>13.2±0.2</td>
<td>26.3</td>
<td>18.0</td>
<td>39.4</td>
</tr>
<tr>
<td></td>
<td>31.6</td>
<td>0.64±0.00</td>
<td>3.1±0.2</td>
<td>21.7</td>
<td>18.8</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.80±0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MoS$_2$-Li</td>
<td>0.1</td>
<td>2.28±0.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.77±0.02$^*$</td>
<td>84.0±7.6</td>
<td>28.2</td>
<td>3.9</td>
<td>112.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.81±0.10$^*$</td>
<td>81.5±6.5</td>
<td>27.8</td>
<td>4.8</td>
<td>109.2</td>
</tr>
<tr>
<td></td>
<td>31.6</td>
<td>1.63±0.11$^*$</td>
<td>11.3±2.5</td>
<td>55.9</td>
<td>27.4</td>
<td>67.2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.78±0.17$^*$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ $M_E$: % of mass of MoS$_2$ in effluent of mass injected

$^b$ $M_D$: % of mass of MoS$_2$ deposited in the column and collected from the column dissection

$^c$ $M_R$: % of MoS$_2$ remobilized after DI injection of average retained mass from triplicate experiments

$^d$ $M_T$: % of total mass ($M_E + M_D$) of MoS$_2$ in effluent ($M_E$) plus mass collected from column dissections ($M_D$)

*: Significant difference (P < 0.05) in fractal dimension compared to 0.1 mM KCl

It was anticipated that the increase in IS would decrease the electrostatic double layer repulsion between the MoS$_2$ NPs and therefore result in the increased aggregation as has been reported in other nanoparticle studies (42-45) with TiO$_2$, ZnO, and CeO$_2$. However,
it was unknown how these effects of IS would vary amongst the two types of MoS$_2$ characterized in this study or at what IS would cause significant change. In general, the MoS$_2$-PL and MoS$_2$-Li became less stable (as observed by an increase in effective diameter and a decrease in EPM) as a function of IS. The average effective hydrodynamic diameters of the MoS$_2$-Li and MoS$_2$-PL were measured in DI water and were 345±4 and 81±1 nm, respectively. A significant effect (P<0.05) of IS on the effective diameter of MoS$_2$-Li did not occur until 31.6 mM KCl was achieved when the diameter increased from 340±13 to 1795±413 nm, respectively. Furthermore, the MoS$_2$-Li effective diameter increased almost by an order of magnitude from 340±13 nm to 3057±402 nm, across the range of 0.1 to 100 mM KCl. This increase in MoS$_2$-Li aggregate diameter as a function of IS is likely a result of the decrease in electric double layer repulsion at higher IS and is in agreement with previous studies performed with carbon nanotubes (46). However, the effective diameter of the MoS$_2$-PL remained fairly constant (81±7 nm) across the IS range tested, and only increased by ~17% from 0.10-100 mM KCl. This was expected as a result from the pluronic surfactant coating on the MoS$_2$ which limited its aggregation as a function of IS. Similar results have been reported for other engineered nanomaterials (e.g., fullerenes (47), and TiO$_2$ (48)) coated with natural organic matter where an increase in particle stability (as observed by a reduction in effective diameter) was reported as a function of NOM concentration.

Similar to the effects of IS on the effective diameter, it was expected that increasing the IS would decrease the overall EPM for both types of the MoS$_2$ as has been
observed previously in the Chen et al. study (49) As a baseline (lowest IS), the EPMs of MoS$_2$-Li and MoS$_2$-PL were measured in DI water and were -3.8±0.1 and -1.8±0.0 ($10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$), respectively. Similar IS conditions that influenced the effect on size for both types of MoS$_2$ were observed regarding the influence on EPM. For example, the MoS$_2$-Li and MoS$_2$-PL EPMs were not significantly effected until an IS of 31.6 and 10 mM KCl was achieved, respectively. For the MoS$_2$-Li, the EPM decreased from -3.8±0.0 to -2.5±0.4 ($10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$) across the range of 0.1-100 mM KCl. The EPM of the MoS$_2$-PL was also decreased from -1.7±0.1 to -0.3± 0.3 ($10^{-8}$ m$^2$ V$^{-1}$ s$^{-1}$) across the range tested. These behaviors for both types of MoS$_2$ with respect to their sensitivity to IS as observed by their decrease in EPM, are in agreement with traditional Derjaguin-Landau-Verwey-Overbeek (DLVO) theory regarding the stability for colloidal particles (50).

The fractal dimension (FD) was measured as a function of IS at an adjusted pH 5 for both types of MoS$_2$ to see if there exists a correlation between the transport results and the aggregate structure (See Table 4.1). The FD parameter can provide a unique mechanistic explanation to help predict the fate of MoS$_2$ aggregates in aquatic environments. Recent studies (28) have suggested that nanoparticle aggregates with a lower FD have a greater breakup potential during transport in the subsurface. However, this phenomenon has never been tested on two dimensional planar particles like MoS$_2$ before and the results from the FD characterization can be found in Table 4.1. For the MoS$_2$-Li, there was a significant difference (P<0.05) observed from 0.1-1 mM KCl, resulting in the FD decreasing from 2.3±0.2 to 1.8±0.0, which suggests the MoS$_2$-Li
aggregate structure becomes less dense and evenly packed as the IS increases which is in agreement with previous studies (29,51). At 0.1 mM KCl, the FD of 2.3±0.2 correlates with previous studies using particle aggregation simulations (52) which reported a fairly dense aggregate structure with FDs ~2.5. This suggests that at low IS (0.1 mM KCl) the MoS$_2$-Li aggregates are densely packed and less likely to break up during transport in aquatic environments. However, from 1 to 100 mM KCl there was no significant difference and the FD of the MoS$_2$-Li remained constant at 1.7±0.1. Similar results have also been reported for TiO$_2$ NPs, where Chowdhury (28) et al. reported that particles with primary particle size of 6 nm were unaffected by IS. This suggests that the MoS$_2$-Li aggregate structures across the range 1-100 mM KCl are similar as a result from fast initial aggregation. Previous computer simulations and experimental studies (53) with colloids reported that aggregates with a FD~1.8 (as were observed from SLS experiments in this study for MoS$_2$-Li) have a much more open structure (compared to particle aggregates with higher FD) from diffusion limited aggregation (DLA) (30). If the FD (1.7±0.1) measured in this study from 1-100 mM KCl does correlate with an open structure for the MoS$_2$-Li aggregates, this suggests that they will have a greater tendency to break apart during transport in porous media and facilitate greater elution in the packed bed column as a function of IS. In 2012, Jassby (54) et al. also reported that there was only a minor impact on the FD as a function of IS of TiO$_2$ aggregates due to the fused nature of their primary particle structure and this is likely the reason why there was no significant change in FD from 1-100 mM KCl for the MoS$_2$-Li aggregates. As observed in SEM images in Figure 4.11, the MoS$_2$-Li aggregates take on a bundle or tissue like
shape, and their primary effective diameter (345±4 nm as measured by DLS in DI water) are relatively large to begin with. As a result, the packing of MoS$_2$-Li aggregates is limited by its size and morphology, and will not be impacted by additional aggregate-aggregate joining as observed in the Jassby et al. study (27). While the FD characterization for MoS$_2$-Li provided important information regarding potential correlations between the aggregate morphology and future transport trends; there was no specific trend observed for the MoS$_2$-PL aggregates characterized in this study. The FD values for MoS$_2$-PL were all less than one (0.8±0.1) across the IS range tested, suggesting that they are not fractal as a result of their pluronic surfactant which prevents their aggregation.

4.3.2 Packed Bed Column Transport Study

Column experiments were conducted with MoS$_2$-Li and MoS$_2$-PL to investigate the influence of ionic strength on the movement of MoS$_2$ in aquatic environments (e.g., sediment beds) across an environmentally relevant range of conditions (1-31.6 mM KCl at pH 5) and to determine which type of MoS$_2$ would be least mobile in aquatic environments. This specific range of solution chemistries was also chosen since it represents the regions where the most significant effects were observed during particle characterization (DLS and EPM) experiments. The transport results were plotted as breakthrough curves (BTCs) and are found in Figure 4.7 and Figure 4.8. The BTCs represent the concentration of MoS$_2$ eluted normalized by the injection concentration.
(C/C₀) as a function of pore volumes (PV) that flowed through the column and provide a measure for the MoS₂ transport in porous media.

**Figure 4.7:** Packed bed column transport results for MoS₂-PL as a function of ionic strength. (A) 0-10 Pore volumes: breakthrough curves as a function of IS (1-31.6 mM KCl) are an average of triplicate measurements with error bars indicating one standard deviation. (B) 10-22 Pore volumes: breakthrough curve after DI was injected to determine the amount of MoS₂-PL reversibly bound.

The shapes of the BTCs also provide critical information to understand the potential deposition or retention mechanisms (e.g., blocking, straining, ripening) that may be occurring during transport. The normalized MoS₂ concentration (C/C₀) was also examined and compared at each IS for MoS₂-PL and MoS₂-Li to identify which type of MoS₂ would be least mobile in sand columns.
Figure 4.8: Packed bed column transport results for MoS$_2$-Li as a function of ionic strength. (A) 0-12 Pore volumes: breakthrough curves as a function of IS (1-31.6 mM KCl) are an average of triplicate measurements with error bars indicating one standard deviation. (B) 12-24 Pore volumes: breakthrough curve after DI was injected to determine the amount of MoS$_2$-Li reversibly bound.

In addition, the overall mass of MoS$_2$-PL and MoS$_2$-Li deposited in the column during transport was determined by integrating under the BTCs after each transport experiment and the results are shown in Table 4.1. Overall the deposition of MoS$_2$-Li and MoS$_2$-PL in the column increased for both nanomaterials as a function of IS, however, a significant effect was observed at different conditions dependent on the type of MoS$_2$. Specifically, no significant effect (P>0.05) on MoS$_2$-Li transport was observed until an IS of 31.6 mM KCl was achieved which and the mass deposited was greater compared to the MoS$_2$-PL. For example, at 10 mM KCl the C/C$_0$ value was ~0.95 for the MoS$_2$-Li while at the same IS, the C/C$_0$ value for the MoS$_2$-PL was ~0.20. This difference was clearly observed.
between the two types of MoS$_2$ at 31.6 mM KCl where 87.9$\pm$2.5\% and 96.0$\pm$0.2\% of the particles were retained in the column for the MoS$_2$-PL and MoS$_2$-Li, respectively. This increase in deposition for the MoS$_2$-PL is interesting since these particles are roughly 19 times smaller than the MoS$_2$-Li counterpart. One might expect a greater retention in the column as the effective diameter of the aggregates increase due to the straining mechanism which suggests particles are retained and cannot pass through regions of the pore spaces due to their large size (55, 56). Straining can occur when the straining parameter ($d_{\text{particle}}/d_{\text{quartz}}$), which is the diameter of the particle ($d_{\text{particle}}$) divided by the diameter of the quartz collector ($d_{\text{quartz}}$), reaches the theoretical threshold of 0.0002 (55, 57). Straining has been used in the past during similar column transport studies to help explain removal mechanisms observed for latex particles (58), non-spherical colloids (59), and other two-dimensional nanomaterials (graphene oxide) (60). For MoS$_2$-PL, the effective diameter at the highest IS (31.6 mM KCl) correlated with a straining parameter ($d_{\text{MoS}_2}/d_{\text{quartz}}$) of 0.0003, which is almost an order of magnitude below the theoretical limit of 0.002 where straining can occur. This suggests that an alternate retention mechanism is likely occurring that is responsible for the MoS$_2$-PL retention during transport in porous media. The breakthrough curve (BTC) observed for the MoS$_2$-PL at 10 mM KCl has been observed before in other transport studies and suggests that either blocking or straining is occurring. Blocking has been used in traditional colloid literature (41, 42) to explain the deposition of colloids during transport in porous media. Blocking occurs when the particles entering the column undergo an initial rapid deposition on available collector sites, followed by a decrease in deposition rate as more deposition sites on the collectors
become unavailable (61, 62). Since the straining parameter is well below the theoretical limit, this suggests that blocking is the dominant removal mechanism during MoS₂-PL transport in porous media. As observed by the BTC shape in Figure 4.7, at 10 mM KCl the MoS₂-PL undergo some massive initial deposition on the empty attachment sites located on the quartz collectors as they enter the column in the first cm, and then after these sites are blocked, a decrease in deposition occurs resulting in more MoS₂ being eluted from the column as a function of time. For the MoS₂-Li transport experiments, the blocking shape was not observed from the BTCs suggesting that straining may be the dominant removal mechanism during transport. This is in agreement with the straining parameter \( \left( \frac{d_{\text{MoS}_2}}{d_{\text{particle}}} = 0.006 \right) \) calculated for MoS₂ at 31.6 mM KCl. From the transport experiments it is clear that each type of MoS₂ undergo unique interactions with the quartz collectors during transport with the MoS₂-PL being the least mobile as compared with MoS₂-Li under similar conditions.

### 4.3.3 Remobilization of MoS₂

To further understand the possibility of remobilization or irreversible attachment, and to identify mechanisms by which particles are being retained (as observed from the transport experiment results described above) for MoS₂-Li and MoS₂-PL, DI water was injected for ~12 pore volumes following a column experiment at each IS. This results in the IS strength being reduced in the column and helps to shed light on the possible mechanisms responsible for attachment, deposition, and remobilization during transport. The results from this “release” portion of the experiments are shown in Figure 4.7B and
Figure 4.8B for MoS$_2$-PL and MoS$_2$-Li, respectively, and have been included in Table 4.1. The amount of mass remobilized (collected in the effluent) after the injection of DI water was divided by the amount that was retained in the column and multiplied by 100 to obtain the mass % remobilized ($M_R$). For the MoS$_2$-Li particles, the $M_R$ increased from 4-27% across the IS range tested suggesting electrostatic interactions are occurring with the quartz collectors during transport and responsible for retention in the column. The limited remobilization as a function of reduced IS also agrees with the FD results observed for MoS$_2$-Li aggregates which showed a sensitivity to IS below 1 mM KCl. This suggests that as the IS was decreased by injecting DI water following an experiment, the MoS$_2$-Li formed densely packed aggregates and became less likely to break up during transport and more likely to be strained out in the narrow pores of the sand column. For the MoS$_2$-PL, however, the $M_R$ remained constant (18.5±0.5%) across the IS range tested suggesting a maximum remobilization regardless of IS. This difference in remobilization phenomena between the two types of MoS$_2$ suggests that the PF-87 pluronic surfactant on the MoS$_2$-PL is interacting with the quartz collectors, resulting in a strong bond and a limited $M_R$. The interactions between the PEO functional groups present on the MoS$_2$-PL surface and the Si function groups on the quartz collector are likely forming strong intermolecular bonds and resulting in irreversible attachment. This irreversible attachment was not observed in other two-dimensional planar particles (i.e., graphene oxide) that exhibited ~100% remobilization once DI water was injected during the release portion of a column experiment (23, 63). The release experiments highlight the different behaviors for MoS$_2$ during transport in sand columns; with MoS$_2$-PL being least sensitive
to change in IS and less mobile compared to MoS$_2$-Li when the remobilization (M$_R$) parameter was considered at similar conditions.

4.3.4 Spatial Distribution of MoS$_2$ in the Column

To provide additional insight into the unique differences observed in the transport and release experimental results between the two types of MoS$_2$: the distribution of MoS$_2$ deposited at each cm during transport was quantified using previously described methods (23) and is reported in Figure 4.9. Overall the majority of MoS$_2$-Li was equally distributed throughout each cm of the column for at the lower IS (1-10 M KCl) tested. However, once 31.6 mM KCl was achieved, a sharp increase (~7 times greater compared to 1 mM KCl condition) in MoS$_2$-Li mass deposited in the top cm of the column was observed as seen in Figure 4.9B.
Figure 4.9: Retention profiles created from the column dissections after a transport experiment in the packed bed column at 1, 10, and 31.6 mM KCl. (A) MoS$_2$-Li retention profile. (B) MoS$_2$-PL retention profile.

This increase in deposition in the top cm of the column correlates well with the effective diameter (~1512 nm at 31.6 mM KCl) characterized in the DLS experiments, which results in a straining parameter ($d_{MoS_2}/d_{quartz}$) of 0.005, suggesting that straining is the removal mechanism occurring at this condition. However, for the MoS$_2$-PL there was no significant difference (P>0.05) in spatial distribution as a function of IS. The retention profiles were very similar across the range of IS tested (1-31.6 mM KCl). The equal spatial distribution of MoS$_2$-PL in the retention profiles suggest that the they are being irreversibly attached to the quartz collectors and is in agreement to the trend observed during the release portion of the column experiments.
4.3.5 DLVO Theory

DLVO theory was used to identify whether the trends observed during the column transport experiments were due to MoS$_2$-quartz interactions (blocking) or MoS$_2$-MoS$_2$ interactions (straining). Calculations were performed using traditional DLVO theory (54, 64) to simulate MoS$_2$-quartz interactions, assuming a constant potential and sphere-plate geometry (65) as seen in Tables 4.2-4.3.

Table 4.2: Results from calculations based upon DLVO and the sphere-plate assumption for MoS$_2$-Li nanoparticles and quartz collectors.

<table>
<thead>
<tr>
<th>IS (M KCl)</th>
<th>Zeta Potential of MoS$_2$ (mV)</th>
<th>Zeta Potential of Quartz (mV)</th>
<th>1° energy barrier (kT)</th>
<th>1° energy barrier separation distance (nm)</th>
<th>2° min depth (kT)</th>
<th>2° min separation distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3}$</td>
<td>-52.4±3.2</td>
<td>-28.6±2.0</td>
<td>260.4</td>
<td>2.5</td>
<td>-0.018</td>
<td>109.5</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>-50.7±1.7</td>
<td>-13.6±0.5</td>
<td>52.8</td>
<td>2.5</td>
<td>-0.32</td>
<td>24</td>
</tr>
<tr>
<td>$10^{-1.5}$</td>
<td>-41.7±1.0</td>
<td>-11.3±1.4</td>
<td>97.6</td>
<td>2.0</td>
<td>-5.7</td>
<td>10</td>
</tr>
</tbody>
</table>

Average hydrodynamic diameter values for MoS$_2$-Li were experimentally recorded and were used in the DLVO calculations.

Electrophoretic mobility (EPM) values for MoS$_2$-Li were used to calculate zeta potentials via the Smoluchowski equation.

The MoS$_2$-Li interaction energy profile at 31.6 mM KCl suggest that a secondary minimum (~5.7 kT) exists at 10 nm. This secondary minimum at 31.6 mM KCl may help explain why there was twice as much deposition in the column compared to the 1 mM KCl condition. For the MoS$_2$-PL DLVO profiles, there was only a small energy barrier (1.9 kT) at 10 mM KCl and no energy barrier at 31.6 mM KCl observed. This absence of

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an energy barrier for MoS$_2$-quartz surfaces at 31.6 mM KCl likely contributed to the fraction (26%) of irreversibly bound particles retained in the column following the release portion of the transport experiments. This is also in agreement with what was observed in the retention profiles where 78% of the MoS$_2$-PL particles remained on the quartz collectors even after being chemically (reduction in IS) and physically (vortexed) perturbed.

**Table 4.3:** Results from calculations based upon DLVO and the sphere-plate assumption for MoS$_2$-PL nanoparticles and quartz collectors.

<table>
<thead>
<tr>
<th>IS (M KCl)</th>
<th>Zeta Potential of MoS$_2$ (mV)</th>
<th>Zeta Potential of Quartz (mV)</th>
<th>1$^o$ energy barrier (kT)</th>
<th>1$^o$ energy barrier separation distance (nm)</th>
<th>2$^o$ min depth (kT)</th>
<th>2$^o$ min separation distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-1}$</td>
<td>-21.0±1.8</td>
<td>-28.6±2.0</td>
<td>24.1</td>
<td>2.0</td>
<td>-0.005</td>
<td>95.5</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>-11.4±1.0</td>
<td>-13.6±0.5</td>
<td>1.9</td>
<td>2.5</td>
<td>-0.13</td>
<td>16</td>
</tr>
<tr>
<td>$10^{-1.5}$</td>
<td>-5.3±1.1</td>
<td>-11.3±1.4</td>
<td>None (-2.6)</td>
<td>2.0</td>
<td>None</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Average hydrodynamic diameter values for MoS$_2$-Li were experimentally recorded and were used in the DLVO calculations.

Electrophoretic mobility (EPM) values for MoS$_2$-Li were used to calculate zeta potentials via the Smoluchowski equation.

To further explain the transport results observed in this study, MoS$_2$-MoS$_2$ interactions were considered and additional DLVO interaction energy profiles were created (Tables 4.4-4.5). A secondary energy minimum (-1.8 kT at 15 nm) was observed for the MoS$_2$-Li at 31.6 mM KCl, which correlates with the straining parameter (0.006) that was calculated and the seven fold increase (compared to the 1 mM KCl condition) in mass...
deposited in the first cm as observed in the retention profiles. A similar trend was observed in previous reports (24, 60, 63) for another two dimensional nanomaterial (graphene oxide), and it was reported that the existence of a secondary minimum contributed to the removal of graphene oxide particles during transport via reversible chemical (electrostatic) interactions. For the MoS$_2$-PL a secondary minimum was not observed when MoS$_2$-MoS$_2$ interactions were considered.

**Table 4.4:** DLVO results based upon the sphere-sphere assumption for MoS$_2$-Li nanoparticles.

<table>
<thead>
<tr>
<th>IS (M KCl)</th>
<th>Zeta Potential of MoS$_2$ (mV)</th>
<th>$1^{st}$ energy barrier (kT)</th>
<th>$1^{st}$ energy barrier separation distance (nm)</th>
<th>$2^{nd}$ min depth (kT)</th>
<th>$2^{nd}$ min separation distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3}$</td>
<td>-52.4±3.2</td>
<td>633.0</td>
<td>0.5</td>
<td>-0.1</td>
<td>127.5</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>-50.7±1.7</td>
<td>545.3</td>
<td>0.5</td>
<td>-0.1</td>
<td>31.5</td>
</tr>
<tr>
<td>$10^{-1.5}$</td>
<td>-41.7±1.0</td>
<td>1413.1</td>
<td>0.5</td>
<td>-1.8</td>
<td>15.0</td>
</tr>
</tbody>
</table>

Average hydrodynamic diameter values for MoS$_2$-Li were experimentally recorded and were used in the DLVO calculations.

Electrophoretic mobility (EPM) values for MoS$_2$-Li were used to calculate zeta potentials via the Smoluchowski equation.

Overall, DLVO interaction energy profiles helped provide additional information regarding the individual removal mechanisms for each type of MoS$_2$ during transport in sand columns. Specifically, the application of DLVO supports the claim that straining is the dominant mechanism for retention in porous media occurring at higher IS for MoS$_2$-Li due to secondary energy minimums present which results in aggregation of the MoS$_2$-
MoS$_2$ particles. Furthermore, the application of DLVO helps support the mechanistic explanation that MoS$_2$-PL likely undergoes irreversible attachment to the quartz collectors due to the absence of (or minimal) energy barriers present during interactions with quartz collectors resulting in the blocking mechanism dominating its removal during transport in porous media. This is in agreement with the trends observed in the limited remobilization ($M_R = 18.6\pm0.5\%$) during release experiments and the equal spatial distribution of MoS$_2$-PL throughout the column in the retention profiles.

**Table 4.5:** DLVO results from calculations assuming sphere-sphere interactions for MoS$_2$-PL nanoparticles.

<table>
<thead>
<tr>
<th>IS (M KCl)</th>
<th>Zeta Potential of MoS$_2$ (mV)</th>
<th>$1^{st}$ energy barrier (kT)</th>
<th>$1^{st}$ energy barrier separation distance (nm)</th>
<th>$2^{nd}$ min depth (kT)</th>
<th>$2^{nd}$ min separation distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3}$</td>
<td>-21.0±1.8</td>
<td>19.7</td>
<td>1.5</td>
<td>-0.003</td>
<td>95.0</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>-11.4±1.0</td>
<td>2.9</td>
<td>2.0</td>
<td>-0.06</td>
<td>19.0</td>
</tr>
<tr>
<td>$10^{-13}$</td>
<td>-5.3±1.1</td>
<td>None (-1.8)</td>
<td>2.0</td>
<td>None</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Average hydrodynamic diameter values for MoS$_2$-Li were experimentally recorded and were used in the DLVO calculations.

Electrophoretic mobility (EPM) values for MoS$_2$-Li were used to calculate zeta potentials via the Smoluchowski equation.

### 4.3.6 SEM Images of Quartz Sand and MoS$_2$

SEM images were taken to better understand the role of physical interactions between the MoS$_2$ and sand grains as a function of their different surface morphologies and to identify any potential physical removal mechanisms during transport. The SEM
images shown in Figures 4.10-4.13 suggest that the physical geometry (two dimensional-planar-flakes) of the MoS₂ likely plays an important role during transport through porous media. It is likely that the planar MoS₂ particles get wedged or removed during transport since their shape and size allow them to interact with the rough surface of the quartz sand. As seen in Figure 4.10A and 4.10D, the surface of the quartz collectors is very heterogeneous with craters and pits ranging from 1-2 microns in diameter.

**Figure 4.10:** Scanning Electron Microscopy (SEM) images taken at different magnifications for quartz collectors, and MoS₂-Li, and MoS₂-PL particles used in the packed bed column experiments. (A, D) Quartz collector at 10 and 5 microns. (B, E) MoS₂-Li at 10 and 1 microns. (C, F) MoS₂-PL at 10 and 1 microns.

In addition, the MoS₂-Li (Figure 4.10B and 4.10E) and MoS₂-PL (Figure 4.10C and 4.10F) SEM images taken highlight the unique two dimension planar-sheet like structure of the MoS₂ particles. As a result of this geometry, van der Walls forces would have a
greater influence since the large surface area of the MoS₂ is able to interact with the surface of the quartz surfaces. This is consistent with the DLVO calculations that revealed an absence in energy barrier for MoS₂-PL and quartz surfaces, and may explain why there was greater MoS₂-PL retention in the column during transport compared to MoS₂-Li even though the size (as measured in DLS experiments) was ~19 smaller at 31.6 mM KCl. Furthermore, it is likely that the both types of MoS₂ are experiencing some wedging or straining as they transport through the column and interact with the rough surfaces on the quartz collectors. This assumption is consistent with others who have reported that wedging and straining are the mechanistic basis for colloid retention during transport in porous media (56, 57, 66).

**Figure 4.11:** SEM images taken at different magnifications of the MoS₂-PL nanoparticles used in this study.
Figure 4.12: SEM images taken of the MoS$_2$-Li nanoparticles used in this study.
Figure 4.13: SEM images of the quartz sand collectors used as porous media in the packed bed column during transport experiments.

4.4 Environmental Implications

This study highlights the different fate and transport mechanisms for two common types of MoS$_2$ in aquatic environments. A comprehensive study was performed to identify the unique behaviors of MoS$_2$-Li and MoS$_2$-PL in aqueous environments so that more information would be gained to understand which type of MoS$_2$ would be least mobile and likely be exposed to various aquatic species (e.g., benthic feeders) in sediment beds. Traditional methods used to synthesize MoS$_2$-Li may result in increased transport in
sediment beds and aquatic systems under environmentally relevant conditions (1-10 mM KCl). However, at higher IS (≥31.6 mM KCl), MoS$_2$-Li will become less stable and aggregate to sizes greater than 1.5 microns. Under these conditions, MoS$_2$-Li will likely be removed via straining and as a result of secondary minimum interactions in sediment beds and may potentially bio-accumulate in benthic organisms. However, the MoS$_2$-PL will tend to transport farther in aqueous systems due to its stable characteristics at environmental conditions (pH 5-9). However, if MoS$_2$-PL comes into contact with quartz media in the subsurface, it will have a higher affinity to be deposited and attach as a result of the reduced energy barrier between MoS$_2$-PL + quartz surfaces as observed from transport experiments and column dissections in this study. Additionally, as observed in the SEM images, the two-dimensional planar geometry of both types of MoS$_2$ nanomaterials will likely contribute to the physical removal of individual flakes during transport in porous media as a result of being wedged into heterogeneous pits present on quartz surfaces. As a result of the chemical and physical mechanisms contributing to the removal during transport in porous media, this study confirms that MoS$_2$-PL will be the least mobile type of MoS$_2$ in aquatic environments compared to MoS$_2$-Li.
4.5 References


(12) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F., Atomically Thin \( <span class="aps-inline-formula">\text{math} \end{math} \)


Chapter 6

Summary and Conclusions
The purpose of this doctoral work was to systematically investigate the effects of environmentally relevant parameters on the fate, and transport of novel engineered nanomaterials (ENMs) and to shed light on the mechanisms responsible for their stability, deposition, retention, and remobilization during transport in aquatic environments. Three different ENMs were used in this study to address specific research objectives set forth in this doctoral research. The fate and transport of graphene oxide nanoparticles (GONPs) were investigated as a function of solution chemistry including the effects of ionic strength, pH, presence of natural organic matter, water type (groundwater and surface water), and presence of divalent cations. The fate and transport of molybdenum disulfide (MoS\textsubscript{2}) was also studied in two forms (lithiated (MoS\textsubscript{2}-Li) and pluronic (MoS\textsubscript{2}-PL)) across a wide range of solution chemistries including investigating the effects of ionic strength and pH.

As described in Chapter 2, the effects of solution chemistry on the fate and transport of GONPs was investigated. Size and surface charge characterization measurements revealed that GONPs are not significantly affected by change in pH across an environmentally relevant pH range of 5-9. At unadjusted pH conditions, it was determined that GONPs become unstable (as measured by increase in hydrodynamic diameter and decrease in electrophoretic mobility) beginning at 31.6 mM KCl. Packed bed column transport experiments confirmed the sensitivity of GONPs to ionic strength (IS) beginning at 31.6 mM KCl, where an increase in particle retention was observed with ionic strength. In addition, it was observed that straining was a contributing physical
removal mechanism for GONPs during transport. Column dissections revealed that the majority of GONPs were removed by straining in the first cm of the column. However, once DI was injected following particle injection for select transport experiments, ~100% of the GONPs were remobilized. DLVO simulations considering particle-particle and particle-quartz interactions were conducted and suggested that reversal of weak secondary energy interactions are likely responsible for the significant remobilization of GONPs. The results from this chapter highlight the dramatic influence IS will have on the fate and transport of GONPs in aquatic environments.

In Chapter 3 a comprehensive experimental matrix was developed to build upon the initial findings in Chapter 1 and to approach real aquatic conditions found in the environment. Solution chemistry parameters (i.e., presence of natural organic matter and presence of a complex assortment of ions) that are ubiquitous in aquatic environments were considered to identify specific contributions of constituents in groundwater and surface waters to the retention, deposition, and remobilization of GONPs. The increasing presence of natural organic matter (NOM) – using Suwannee River Humic Acid as a model organic – further stabilized the GONPs in both monovalent ($\text{KCl}$) and divalent ($\text{CaCl}_2$) salts due to steric repulsion forces. Additionally, the presence of NOM resulted in greater GONP transport in the packed bed column. Divalent cations ($\text{Mg}^{2+}$ and $\text{Ca}^{2+}$) were observed to reduce the stability (as observed in an increase in hydrodynamic diameter and decrease in electrophoretic mobility) of GONPs as a function of IS. Specifically the presence of ($\text{Ca}^{2+}$) ions were observed to undergo bridging effects with
the oxygen functional groups (carboxyl, hydroxyl, and carbonyl) present on the GONPs surface and basal planes resulting in larger aggregates which in turn reduced their transport in the packed bed column. When synthetic groundwater and surface water suspensions were compared, it was determined that GONPs were more stable in surface waters resulting in smaller aggregates and increased transport in the column. The reduced stability and transport in groundwater suspensions is likely attributed to the increased (2x greater) hardness (Mg$^{2+}$ and Ca$^{2+}$) present in that system. Overall, the findings from Chapter 3 suggest that GONPs are likely to settle out and be less mobile in groundwater environments as a result from the limited amounts of NOM and higher concentrations of divalent cations present. Conversely, in surface water environments where GONPs are in contact with significantly greater amounts of NOM and only minor amounts of divalent cations, their transport is likely to be greater. This increased transport in surface waters may result in potential bioaccumulation by aquatic organisms as they come in direct contact with GONPs in water columns or sediment beds of rivers and lakes.

Chapter 4 included an investigation into a novel two dimensional transitional metal dichalcogenide that has been rivaling graphene in regards to potential future electrochemical applications. The fate and transport of two forms (lithiated (MoS$_2$-Li) and pluronic (MoS$_2$-PL)) of molybdenum disulfide (MoS$_2$) were studied to investigate which form would be least mobile in aquatic environments. It was determined that while a pluronic (PF-87) coating on the MoS$_2$ increased the stability (as measured in only a minor increase in hydrodynamic diameter as a function of IS), the transport
through the packed bed column was dramatically reduced as compared to the lithiated form. The MoS$_2$-PL was observed to have a much greater retention in the packed bed column compared to the MoS$_2$-Li at similar IS (1-31.6 mM KCl) even though the MoS$_2$-Li aggregates were much greater for all conditions tested. Fractal dimension (FD) measurements were taken for both types of MoS$_2$ to help identify any correlation with the transport results in the column. It was determined that application of static light scattering to MoS$_2$-PL is limited as a result from their pluronic coating which reduced any aggregation in aqueous suspensions resulting in fractal dimension values below the theoretical limit (<1). However, MoS$_2$-Li did show a sensitivity to IS and a reduced FD was observed from 0.1-1.0 mM KCl suggesting that rapid aggregation occurs at higher IS which results in more open (or ‘stringy’) aggregates and may help explain why there was greater remobilization observed for MoS$_2$-Li compared to MoS$_2$-PL.

Furthermore, scanning electron microscopy (SEM) images helped to shed light on additional physical removal mechanisms for both types of MoS$_2$ during transport. SEM images revealed that heterogeneities on the quartz collectors may result in MoS$_2$ becoming “wedged” into crater like pores on the quartz surface during transport. DLVO calculations were also considered to shed light on the chemical mechanisms for retention or attachment during transport. MoS$_2$ particle-collector interaction energy profiles suggest that the absence of an energy barrier between these two surfaces is likely the reason why limited remobilization occurred during MoS$_2$-PL transport experiments. It is likely that the surface chemistry present on the MoS$_2$-PL is contributing to the specific
DLVO interactions between the triblock copolymer (PF-87) and the quartz collectors. Overall, it was determined that the PF-87 coating will result in the pluronic form of MoS$_2$ being less mobile in aquatic environments.

The results from this doctoral study provide the following important information regarding predicting and understanding the behavior of ENMs in aquatic environments: First, traditional colloid filtration theory can be used to help predict the fate and transport of two dimensional (sheet-like) nanomaterials in aquatic environments. Second, the unique solution chemistry parameters (ionic strength, pH, presence of natural organic matter, divalent ions) present in different aquatic environments will correlate with specific GONPs and MoS$_2$ behavior (deposition, retention, and remobilization). Third, the use of traditional DLVO theory is crucial in describing transport results in the packed bed column and understanding the unique surface interactions between two dimensional planar ENMs (GONPs and MoS$_2$) and quartz collectors during transport. Fourth, the pluronic form of MoS$_2$ will be the least mobile in the aquatic environment as observed by the significant retention of MoS$_2$-PL during transport in the packed bed column. Finally, the dominant physical removal mechanisms for the two dimensional ENMs will be “straining” and “wedging” due to the influence of ionic strength on the aggregate size and the planar geometry for GONPs and MoS$_2$.

While this doctoral research investigated two novel or “boutique” ENMs (GONPs and MoS$_2$), there still exists a large demand for more fate and transport studies on other emerging ENMs (e.g., transitional metal dichalcogenides). Moreover, there
needs to be a concerted effort to take all of these fate and transport studies to create a predictive, quantitative-structure-activity-relationship (QSAR) approach to understand the fate of all ENMs, and this doctoral work is one of the first to do this. Currently, there are big breakthroughs occurring in the field of material science which are allowing for the synthesis and production of novel nanomaterials almost every week. This large influx of new ENMs into the global market and industrial applications will produce a huge challenge for policy makers and international regulators who are trying to determine which ENMs to regulate and which ones to stamp for approval. While this doctoral study has provided some key insights into the behavior of two emerging novel ENMs (GONPs and MoS$_2$) while trying to mimic the environmental conditions found in most natural waters, future studies should consider adding more complex parameters (presence of bacteria, different forms of natural organic matter, anaerobic conditions, seasonal variances in solution chemistry) over a longer period of time (>1 year) to capture the unique dynamics that actually occur in nature. This type of study would be expensive and time consuming but would provide a comprehensive set of data for the scientific community to understand the complex interactions between ENMs and the environment and to determine which ENMs will be the most toxic and under what conditions so that the benefits of nanotechnology can be maximized while the potential negative consequences can be reduced.

The findings in this doctoral research can be used to understand and manage ENMs once they enter aquatic environments and have the following
implications. First, engineers will be able to manage current wastewater treatment facilities by understanding what conditions will facilitate a pulse of ENMs entering the system. For example, since GONPs become ~100% remobilized at environmental ionic strengths (<10 mM), engineers at the wastewater treatment plans (WWTP) will know how to prepare the coagulant dosage for the influent based on the spike in ENM contaminants entering the WWTP following a rain event. Second, the ability to predict the fate and transport for GONPs and MoS$_2$ based on the solution chemistry present in different natural waters will allow for fast and efficient remediation of future environmental spills should they occur. Third, this study will provide critical information to help future policy makers and regulators to make informed decisions based on which type of ENMs will be least mobile in the environment. For example, this study has shown that while pluronic coatings stabilize the size and surface charge of ENMs; the transport will be dramatically reduced due to the unique interactions between the pluronic surfactant and quartz sand. Finally, this doctoral research provides a complex data set over a wide range of environmentally relevant parameters for multiple forms of ENMs that can be used to help promote “green synthesis” for future ENMs. For example, by understanding the mechanisms that dominate the fate and transport for each type (carbon based or transitional metal di-chalcogenides) of ENMs being synthesized, materials scientists will have direct control over what form of nanomaterial an aquatic organism (e.g., phytoplankton) will likely come in contact with in aquatic systems, and thereby have the ability to reduce harmful impacts to the environment.